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Valorization of coffee byproducts via biomass conversion technologies

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DEDICATION

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Abstract

Koffie is een van de belangrijkste landbouwproducten ter wereld, vooral omwille van het gebruik als drank. Het is een zeer populair product, dat dagelijks wordt genuttigd door miljoenen mensen; het is het op een na meest verhandelde product ter wereld, na petroleum. Niettemin gaat de productie van koffie gepaard met grote hoeveelheden bijproducten, tijdens de behandeling van vrucht tot consumptie. Afvalproducten van koffie en bijproducten verkregen tijden het verwerken van koffiebonen zijn een bron van ernstige vervuiling, wat voor milieuproblemen zorgt in koffie producerende landen. Tenzij behandeld vervuilen deze afvalproducten het milieu, beschadigen aquatische ecosystemen, en bedreigen de volksgezondheid en fauna en flora, wat afbreuk doet aan de economische winsten die gemaakt worden door koffieproductie.

De belangrijkste bijproducten die worden gegenereerd zijn vliezen (het omhulsel van de koffieboon, geproduceerd bij droog verwerken van koffiebonen), pulp (bij nat verwerken van koffiebonen), schillen (verkregen wanneer koffie wordt gedroogd en de schil wordt verwijderd), koffiebonen van onvoldoende kwaliteit (niet voldoende of teveel gerijpt), het zilvervliesje (wanneer koffiebonen worden gemalen en geroosterd), en gebruikte koffiebonen (nadat ze zijn gebruikt om de koffiedrank te genereren). Verscheidene pogingen werden ondernomen om de vaste residu fracties te hergebruiken, zoals direct gebruik als brandstof in de landbouw, als veevoeder, voor fermentatie, adsorptie, biodiesel productie, brikettering, samenpersen tot pellets, tannine extractie en productie van gespecialiseerde producten. Het gebruik van bijproducten van koffie is belangrijk vanuit milieu-oogpunt, naast de mogelijke positieve economische waarde van deze bijproducten.

Bijproducten van koffieproductie kunnen door thermochemische of biochemische processen worden omgezet tot biogas, biobrandstof, biodiesel, of bioethanol, of kunnen verbrand worden. Het gebruik van koffieresidus als een bron van bioethanol na natte conversie stelt een uitdaging, omdat lignocellulose zeer resistent is tegen degradatie. Dit wordt onder meer veroorzaakt door cross-linking tussen de polysacchariden cellulose en hemicellulose en lignine via ester en ether bindingen. Om dit te remediëren werden verscheidene voorbehandelingsmethoden bestudeerd, om verschillende types van biomassa te kunnen gebruiken voor bioethanol productie. Geen

enkele van deze methoden is optimaal, omdat elke voorbehandeling haar eigen intrinsieke voor- en nadelen heeft. Er is geen eenvoudige voorbehandelingsmethode beschikbaar voor toepassing op commerciële schaal.

De belangrijkste focus van dit doctoraatsonderzoek is het nagaan van het potentieel van bijproducten van koffieproductie voor valorisatie via technologieën voor conversie van biomassa. Alle vermelde residu fracties (koffievliezen, pulp, schil, zilvervlies, gebruikte koffie en onvolkomen koffiebonen) werden beschouwd. De doelstellingen van de studie waren in de evaluatie van de impact van afvalwater dat wordt geloosd door de koffie-industrie bij nat verwerken, en het onderzoeken van technologische oplossingen voor het verwerken van vaste residus die een toegevoegde waarde kunnen leveren. De technologische screening verkende de haalbaarheid van het gebruik van vaste residus voor de productie van bioethanol, biokool, bio-olie, actieve kool en compost.

Voor het evalueren van de impact van effluenten van traditionele natte koffie verwerking op de stroomafwaartse waterkwaliteit werden stalen genomen van 11 rivieren die worden geassocieerd met natte verwerking van koffie. Kwaliteitsparameters voor het water gebruikt in deze verwerkingseenheden werden gemeten voor inname, tijdens het verwerken zelf, en na het lozen van het effluent. De resultaten geven aan dat het verwerken van koffie een vervuilend effect heeft op de ontvangende rivieren. De variatie in de duur van het weken van koffiebonen, fermentatie van de koffiepulp, en de afwezigheid van aangepaste zuiveringsmethoden waren de belangrijkste factoren geassocieerd met de invloed op de parameters die vervuiling van oppervlaktewater weergeven door de lozingen van koffieverwerkingseenheden. In het algemeen wijken de gemeten warden in belangrijke mate af van zowel de Ethiopische EPA wetgeving en de US-EPA richtlijnen voor waterkwaliteit. Dit suggereert dat verder onderzoek nodig is voor het ontwikkelen van technieken voor valorisatie van afvalstoffen, en behandelingsmethoden met het oog op duurzamen koffieproductie.

Hydrolyse van koffie residus met β-glucosidase enzyme en fermentatie met lignocellulose gisten, gevolgd door opzuivering met pervaporatie resulteerde in een superieure opbrengst aan bioethanol voor gebruikte koffie en vliezen vergeleken met andere fracties. In het algemeen was hydrolyse van koffievliezen met zuur en cellulolytische hydrolyse en fermentatie met

lignocellulose gist GSE16-T18 gevolgd door pervaporatie geschikt bevonden om het aanvaardbare ethanol opbrengst te leveren.

De resultaten van de productie van bioethanol door pervaporatie van het fermentatiemedium van gedroogde koffiepulp bevestigden dat hoewel de opbrengst van fermenteerbare suikers stijgt wanneer de hoeveelheid verdund zwavelzuur hoger is, er een limiethoeveelheid is waarbij de concentratie aan reducerende suikers optimaal is. Bijgevolg werd koffiepulp vermalen en voorbehandeld met verschillende concentraties aan verdund zwavelzuur (0, 1, 2, 3, 4, 5 en 10 vol %) bijverschillende vast/vloeistof verhoudingen (1:1, 1:2, en 1:4). De optimimalisatiestudie geeft aan dat 48 u enzyme hydrolyse en 12 u fermentatie van de stalen met lignocellulose gist GSE16-T18 de beste fermentatietijden geeft bij dewelke de beste ethanol titer (7.03 ± 2.63 g/L) werd verkregen. Pervaporatie van de gefermenteerde voeding concentreerde de ethanol tot 15.47 ± 0.66 g/L. Dit bevestigde dat hydrofobe pervaporatie niet voldoende is voor een adequate zuivering van ethanol. Dit geeft aan dat pervaporatie verder moet worden verbeterd met een verhoogde ethanol selectiviteit.

De studie van compostering gaf aan dat koffievliezen en pulp kunnen gecomposteerd worden, alleen of vie co-composteren met aan de bron gescheiden huishoudelijk afval, wat een zeer mature en stabiele compost leverde met een goede kwaliteit, die voldoet aan de kwaliteitsstandaarden van verschillende landen. De C/N verhouding van gematureerde compost is lager dan 25:1, wat optimaal is. De toevoeging van 1/4 locale aarde (wt/wt) aan een mengsel van compost geproduceerd uit 1/3 koffiepulp, 1/3 bladeren van de banaansoort *Ensete ventricosum*, en 1/3 zacht, droog hout leverde een optimaal gewicht van kool bij veldtesten. In het algemeen kan de geproduceerde compost gebruikt worden voor ungelimiteerde landbouwtoepassingen.

De studie van pyrolyse gaf aan dat meer actieve kool kon worden geproduceerd door pyrolyse van koffiepulp dan bij elke andere fractie van koffie residuds. Zilvervlies en schillen in het bijzonder hebben een hogere opbrengst aan bio-olie dan alle andere koffie residus. Dit impliceert dat ze kunnen gerecycleerd worden bij een goed management van koffie residu fracties. Er kan bijgevolg worden besloten dat valorisatie van koffie residus via non-catalytische pyrolyse een veelbelovend alternatief is om biokool, bio-olie, bio-gas, actieve kool en componenten met

toegevoegde waarde (zoals palmitinezuur, caffeine, linoleenzuur, 1,4-benzeendiol, oliezuur, fenol, methylfenol, tolueen, hexadecaanzuur, 2-methoxy 4-vinylfenol, stigmastan-3,5-diene, indol, dimethoxyacetofenon, methylfenol, tetradecaan, pentadecaan en andere componenten.

Samengevat kan worden gesteld dat de resulten van de fermentatie, pervaporatie, compostering en pyrolyse van koffie residus aangeven dat koffie bijproducten kunnen worden gebruikt voor herwinning van materialen met het oog op duurzame koffieproductie.

Abstract

Coffee is one of the world's most prominent agricultural products, mainly used as a beverage. It is a highly popular product, consumed by millions of people every day and it is the second largest traded commodity in the world after petroleum. However, it generates a large amount of coffee by-products/residues during processing from fruit to cup. Coffee waste products and by-products produced during coffee berry processing constitute a source of severe contamination and pose serious environmental problems in coffee producing countries. Thus, unless treated, coffee waste pollutes water sources, damages aquatic ecosystems, and threatens public health and wildlife, which offsets the economic benefits accrued from coffee production.

The different byproducts that are produced include coffee husk (produced when coffee berries are processed by the dry processing method), coffee pulp (generated during wet coffee processing), parchment (produced when washed coffee is dried and deshelled), defected coffee beans (immature or overripe coffee beans with poor quality), silver skin (produced when coffee beans are milled and roasted), and spent coffee (produced when roasted and ground coffee bean is brewed). Several attempts have been made to re-use the coffee processing solid residues, which include its direct use as fuel in farms, animal feed, fermentation, adsorption, biodiesel production, briquetting, pelletizing, tannin extraction and production of specialty commodities. The use of coffee processing by-products has a critical environmental relevance.

Coffee processing by-products can be converted through thermochemical or biochemical processes into biogas, biofuel, biodiesel, bioethanol or could be directly subjected to combustion. Using coffee waste as a source of bioethanol after wet conversion poses a challenge, because lignocellulosic waste is very resistant to degradation. This is, among others, due to cross-linking between the polysaccharides cellulose and hemicelluloses, and the lignin via ester and ether linkages. For this purpose, various pretreatment technologies have been extensively studied to process different types of biomass for cellulosic bioethanol production. None of these can be considered optimal, because each pretreatment has its intrinsic advantages and disadvantages. No easy pretreatment option is available yet for commercial scale applications.

The main focus of this PhD research is to investigate the potential for valorization of coffee byproducts via biomass conversion technologies. All relevant coffee processing byproducts (coffee husk, pulp, parchment, silver skin, spent coffee and defected coffee bean) have been considered. The main objectives of the study are the evaluation of the impact of waste water produced by wet coffee processing industries, and the screening of waste processing technologies for their potential in processing coffee waste. The technology screening includes the feasibility of coffee waste fractions for producing bioethanol, biochar, bio-oil, activated carbon and compost.

To evaluate the impact of effluents from traditional wet coffee processing plants on the downstream water quality, samples were collected from 11 rivers/streams associated with wet coffee processing plants. Quality parameters of the water used in these plants were measured before intake, during processing and after effluent discharge. The results indicate that the coffee processing mills were polluting streams and rivers. The variation in soaking time of coffee beans, fermentation of the coffee pulp, and the absence of appropriate treatment facilities were the major factors associated with the magnitude of the water pollutant parameters released by the coffee processing plants. In general, the measured values of effluent parameters significantly deviate from both the Ethiopian-EPA and US-EPA surface water quality guidelines. This calls for further research in the design and implementation of coffee waste valorization and treatment in view of sustainable coffee production.

Hydrolysis of coffee waste samples using cellulose complex and β-glucosidase enzymes and fermentation with lignocellulosic yeast, followed by purification using pervaporation resulted in a superior bioethanol yield for spent coffee and husk than for any other coffee waste fraction. In general, husk hydrolysis using acid and cellulolytic hydrolysis and fermentation with lignocellulosic yeast GSE16-T18 followed by pervaporation was found to be viable for producing an acceptable ethanol yield.

The results in the production of bioethanol by pervaporation of the fermentation broth of dried coffee pulp confirmed that even though the yield of fermentable sugar is increasing as the amount of diluted sulfuric acid is increased to a certain extent, there is a limit of diluted sulfuric acid at which the amount of reducing sugar concentration is optimal. Consequently, coffee pulp

was grinded and pretreated with different concentrations of diluted sulfuric acid (0, 1, 2, 3, 4, 5 and 10 vol %) at different solid:liquid ratios (1:1, 1:2, and 1:4). The optimization study indicates that 48 h enzyme hydrolysis and 12 h fermentation of the samples with lignocellulosic yeast GSE16-T18 strain is the best fermentation time at which the best ethanol titer (7.03 ± 2.63 g/L) was obtained. Pervaporation of the fermented feed concentrated the ethanol to 15.47 ± 0.66 g/l. This confirmed that hydrophobic pervaporation is not sufficient to purify ethanol adequately. It also indicates that pervaporation needs to be further improved by enhancing the ethanol selectivity.

The composting study indicates that coffee husk and pulp can be composted alone or co-composted with source separated municipal solid waste, yielding very mature and stable compost with good quality, which is in the range of compost quality standards/guidelines set by different countries. The C/N ratio of matured compost samples is in the optimum range of < 25:1. It was confirmed that the addition of $1/4^{th}$ of local soil (wt/wt) on a mixture of compost produced from $1/3^{rd}$ coffee pulp, $1/3^{rd}$ false banana leaves (*Ensete ventricosum*), and $1/3^{rd}$ soft dry woods yields an optimum fresh head weight of cabbage among all field trials. In general, the produced compost can be used for unrestricted agricultural purposes.

The pyrolysis results indicate that more char and activated carbon could be produced from pyrolysis of coffee pulp than from any other fraction of coffee waste. In particular, the coffee waste fractions silver skin and parchment were found to yield higher bio-oil yield than the other coffee waste fractions. This in turn implies that they can be recycled if there is proper management of coffee waste fractions. Thus, it can be concluded that valorization of coffee waste fractions via non-catalytic pyrolysis is a promising alternative to reclaim bio-char, bio-oil, bio-gas, activated carbon and generation of compounds of added value, for example palmitic acid, caffeine, linolenic acid, 1,4-benzenediol, oleic acid; phenol, methylphenol, toluene, hexadecanoic acid, 2-methoxy 4-vinylphenol, stigmastan-3,5-diene, indol, dimethoxyacetophenone, methylphenol, tetradecane, pentadecane and others.

In summary, the results from the fermentation, pervaporation, composting and pyrolysis of coffee waste fractions indicate that coffee byproducts can be a suitable candidate for resource recovery in view of sustainable coffee production.

List of abbreviations and acronyms

AAS	Atomic absorption spectrometry
AMSIC	African Membrane Society International Congress
BOD	Biological (biochemical) oxygen demand
BY	Baker's yeast
C/N	Carbon to nitrogen ratio
C5 yeast	Lignocellulosic yeast GSE16-T18 strain
CCME	Canadian council of ministers of the environment
CEAP	Concentration of ethanol after pervaporation
COD	Chemical oxygen demand
DCB	Defected coffee bean
DO	Dissolved oxygen
EC	Electrical conductivity
ECTA	Ethiopian coffee and tea development and marketing authority
EFEPA	Ethiopian federal environmental protection authority
FDRE	Federal Democratic Republic of Ethiopia
FTIR	Fourier transform infrared spectroscopy
GC-MS	Gas chromatography–mass spectrometry
HPLC	High performance liquid chromatography
IC	Initial concentration (Feed solution)
LSD	Least significant difference
MC	Moisture content
ND	Not detected
OC	Organic carbon
OM	Organic matter
P1	Centrifugal pump 1
P2	Centrifugal pump 2
PDMS	Polydimethylsiloxane
PERM	Permeate

PFP	Perfluoropolymer
POLYIM	Polyimide
PP	Pervaporation pressure
PT	Pervaporation temperature
PTMSP	Poly (1-trimethylsilyl-1-propyne)
PV	Pervaporation
PVPHILIC	Hydrophilic membrane alternative mode of pervaporation unit
PVPHOBIC	Hydrophobic membrane alternative mode of pervaporation unit
RET	Retentate
S. cerevisiae	*Saccharomyces cerevisiae*
SC	Spent coffee
SOD	Sediment or benthic oxygen demand
SS	Suspended solid
SSMSW	Source separated municipal solid waste
TD-GC/MS	Thermal desorption Gas chromatography–mass spectrometry
TF	Total flux
TGA	Thermogravimetric analysis
TN	Total nitrogen
TSS	Total suspended solid
UDL	Under detection limit
USA	United states of America
USEPA	United states environmental protection authority
VP-PFP	Vapor permeation perfluoropolymer
VS	Volatile solid
XRF	Semi-quantitative elemental analysis

Contents

1. Introduction, scope and outline

1.1 History of coffee and coffee brewing

Coffee is one of the world's most popular beverages and has grown steadily in commercial importance during the last 150 years (Daglia et al., 2000). The word 'coffee' has originated from the Arabic word Quahweh. Today its popularity is identified by various terms in several countries such as café (French and Spanish), caffe (Italian), kaffee (German), koffie (Dutch) and coffee (English) (Smith, 1985). The exact date of *Coffea arabica*'s first departure from its center of origin, Ethiopia to other parts of the world is not precisely documented. However, what is known is that the coffee plant first made its way from Ethiopia to Yemen (Wellman, 1961; Vega, 2008). The stimulatory effects of roasted coffee beans were well known and the Arabs brought *Coffea arabica* seeds from Ethiopia to Yemen (Arabian Peninsula) during the 13th century, and established the first plantation (Monaco et al., 1977). The province of Kaffa in Ethiopia is considered to be the original habitat of Arabica coffee and Central Africa is reckoned to be the native of robusta coffee. With extensive and wide spread cultivation of coffee across the globe, at present Brazil is the largest producer and exporter of coffee in the world (Murthy and Naidu, 2012).

Coffee is one of the world's largest agricultural products used mainly for the purpose of producing beverages. Coffee, one of the most popular beverages, is consumed by millions of people every day. It is the second largest traded commodity in the world after petroleum, and generates large amount of coffee by-products/residues during processing from fruit to cup (Mussatto et al., 2011). It has been estimated by the U.S. Department of Agriculture (USDA) that the world's coffee production reached 8.1 million tons in 2011 (Oliveira et al., 2008). Over 90% of coffee production takes place in developing countries, while consumption is mainly in the industrialized economies (Ponte, 2002). The per capita rate of coffee caffeine use in Canada and the United States is approximately three times that for the world as a whole (Gilbert, 1984).

In addition to coffee wastewater and mucilage (thick and gluey substance which is removed from coffee bean during wet coffee depulping and fermentation processes), processing of coffee generates different byproducts. These are coffee husk (produced when coffee berries are

processed by the dry processing method), coffee pulp (generated during wet coffee processing), parchment (produced when washed coffee is dried and deshelled), defected coffee beans (immature or overripe coffee bean which has poor quality), silver skin (produced when coffee bean is milled and roasted), and spent coffee ground (produced when roasted and grinded coffee bean is brewed).

The consumable form of green coffee beans is obtained after roasting. The quality evaluation of green coffee is based on odor and flavor tests, as well as on the size, shape, color, hardness, and presence of defects (Feria-Morales, 2002). The characteristic flavor and aroma of coffee result from the combination of hundreds of chemical compounds produced by the reactions that occur during roasting and brewing (del Castillo et al., 2002). Coffee brewing is heterophase ranging from smooth pure solution to emulsion (Drip filter coffee, Nordic boiled coffee, Turkish style brew, Espresso, and cappuccinos). Coffee processing is an art as well as science and involves a series of stages each of which has a distinct purpose (Murthy and Naidu, 2012). However, direct large-scale utilization of coffee waste around the world remains a challenge due to the presence of caffeine, free phenols and tannins (polyphenols) (Fan et al., 2003).

1.2 Background of Ethiopian coffee sector

Ethiopia is the birthplace of Arabica coffee *(Coffea arabica L.)*, which covers 66% of the world coffee market (Labouisse et al., 2008). In Ethiopia, coffee is produced by more than 4 million farm households; it provides employment for a quarter of the population (Tefera and Tefera, 2014) and contributes up to 50% of household income for coffee producers (Wiersum et al., 2008). Ninety-five percent of the coffee production in the country is covered by smallholder farmers with land holding size of less than 2 ha (Francom and Tefera, 2016). Coffee production surged over the last two decades (Yadessa, 2014).

1.3 Current coffee production and its challenges

Processing coffee refers to the methods used to transform a picked coffee cherry into a green coffee bean that is ready to be roasted and then being brewed. It includes the steps used to remove the different layers surrounding a coffee bean, the cherry, mucilage and parchment, as well as how beans are dried. There are three main ways that coffee is processed, and each produces unique characteristics. They are dry, wet and semi-washed processing. Using the semi-washed method, aspects of both the washed and unwashed methods are combined. In this process, the outer skins are removed, but the pulp is allowed to remain and dry in the sun. Once the drying process is complete, often the pulp is wet and then the beans are removed just like they are in the dry process. That means, coffee fruits are washed and sorted as in the washed method. However, they are not placed in fermentation tanks, and instead they are set out to dry.

The coffee industry liberates enormous amounts of coffee byproducts that are rich in carbohydrates, proteins, pectins, bioactive compounds like polyphenols and are cheap renewable resources (Murthy and Naidu, 2010). Coffee processing industries are one of the most significant consumers of water and produce large amounts of highly acidic wastewater that contain high concentrations of organic matter, nutrients, suspended matter (Tekle et al., 2015). Depending upon the method of coffee cherries processing, i.e., wet or dry process, roasting and brewing solid residues like pulp, husk, silver skin and spent are obtained. Coffee waste and by-products produced during coffee berry processing constitute a source of severe contamination and pose serious environmental problems in coffee producing countries. Therefore, disposal of coffee pulp is becoming an emerging environmental problem worldwide due to its putrefaction (Corro et al., 2013).

During wet coffee processing, it is practically observed that there is a change in weight of fresh coffee cherry and bean at different stages of coffee processing. For this purpose, a mass balance was made for the fresh and ripe coffee cherry from the wet coffee processing method (taking coffee cherry from Jimma zone, Ethiopia as a reference) and the results are indicated in figure 1.1. The coffee mass balance indicates that during wet coffee processing 1 kg of ripe and

fresh coffee cherry yielded only 60 g (6%) of brewed (soluble) coffee and there are many intermediate byproducts. Similar results were reported by the study of Folmer (2014).

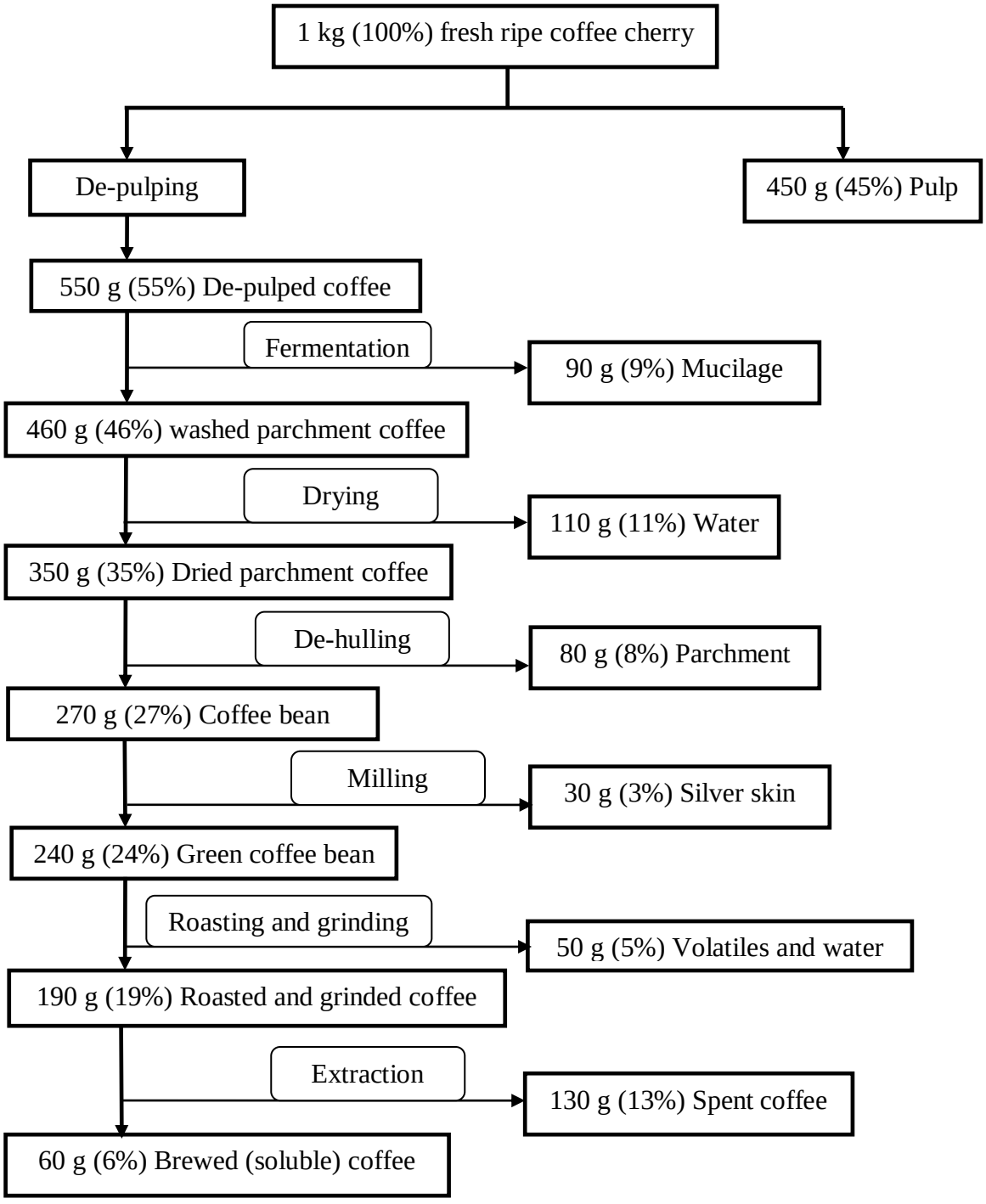


Figure 1.1 Coffee mass balance during wet process from ripe coffee cherry

Coffee husks, which are produced through dry processing, are the major solid residue from the handling and processing of coffee, since for every kg of coffee beans produced, approximately 1 kg of husks are generated (Boccas et al., 1994; Gouvea et al., 2009) and for every 2 tons coffee cherries processed, nearly 1 ton pulp is generated (Adams and Dougan, 1981). Almost 50% of the worldwide coffee produced is processed for soluble coffee preparation (Ramalakshmi et al., 2009). On average one ton of green coffee generates about 650 kg of spent coffee, and about 2 kg of wet spent coffee is obtained for each kg of soluble coffee produced (Pfluger, 1975).

The environmental impacts of coffee are enormous, with large quantities of solid and liquid waste generated globally (Hue et al., 2006). In a life cycle analysis of coffee, Salomone (2003) reported cultivation and consumption of coffee as the two largest contributors of negative environmental impacts. Coffee pulp and processing wastewater represent the two waste streams that most contribute to soil and water contamination. Process water required to obtain clean coffee beans ranges from 5 to 20 L kg^{-1} of beans, with effluent BOD_5 levels increasing from 13 to 11,000 mg L^{-1} (Hue et al., 2006). Water usage for coffee processing by Indian coffee estates varies from 2.25 to 23 m^3 per tonne of fruit processed (ASTRA, 2002a). Coffee pulp and husks also represent a significant soil and water contamination risk through highly degradable components, such as proteins and sugars, and more complex compounds, which may be phytotoxic, e.g., tannins and phenols (Preethu et al., 2007).

Coffee wastes unless treated pollutes water sources, damages aquatic ecosystems, and threats the health of nearby residents and wildlife which offsets the economic benefits accrued from coffee production. Haddis and Devi (2008) assessed the effect of effluent generated from the coffee-processing plant on water bodies and human health in its vicinity and indicated that it caused severe water pollution and illnesses like skin irritation, stomach problem, breathing difficulties, and nausea among downstream users.

1.4 Biomass conversion technologies

The conflict between the increasing energy demand and the depletion of fossil fuels, coupled with the mounting evidence of climate change, needs the diversification of energy sources significantly (Esen and Yuksel, 2013; Yılmaz and Selim, 2013; Kiriyama and Kajikawa, 2014). Plant biomass is currently the only renewable feedstock that may be used for producing hydrocarbon fuels (Kelkar et al., 2015). Biomass, an abundant feedstock source (Demirbaş, 2001; Mandotra et al., 2014), and one of the most promising alternative energy sources, offers many attractive features for fossil resource replacement, including a zero net release of carbon dioxide (Balat, 2011).

Using biomass feedstock from agricultural waste sources for bio-energy production might play a key role, since it will reduce greenhouse gas (GHG) emissions, it will diversify energy sources reducing the oil and gas dependence, and finally, it will provide new production scenarios and alternative sources of income to farmers (Librenti et al., 2010). The energy supply from domestic biomass resources not only enhances fuel diversification but also reduces air pollution because the biomass resource contains relatively low contents of sulfur and heavy metals in comparison with fossil fuels such as coal (Balat, 2007). In this respect, agricultural residues contain large amounts of lignocellulosic constituents (i.e., cellulose, hemicellulose and lignin) and thus possess high-energy contents (Ebeling and Jenkins, 1985). Therefore, they can enrich available carbon sources in the production of biomass energy based on benefits of both energy utilization and environmental protection (Tsai et al., 2012).

Coffee waste can be a source of the most interesting and valuable products, among which metals, oils and fats, lignin, cellulose and hemicelluloses, tannins, antioxidants, caffeine, polyphenols, pigments, flavonoids, through recycling, compound recovery or energy valorization, following the waste hierarchy (Mata, 2018). Applications in the field of industrial residue management promote sustainable development of country's economy (Murthy and Naidu, 2012). A more recent approach has been the use of processing technologies to fractionate potentially high-value components, thereby turning waste streams into value added products (Laufenberg et al., 2003; Wyman, 2003). The recovery of such value-added compounds from

processing byproducts has increased due to their availability. In addition, pertinent amounts of these by-products, which currently remain unexploited, might pose an environmental problem (Wyman, 2003). Thus, the currently adopted valorization steps should lead to the complete exploitation of the by-products and waste biomass, with remarkable enhancement of the environmental and economic sustainability (Murthy and Naidu, 2012).

Biomass can be converted into three main products: two related to energy - power/heat generation and transportation fuels and one as a chemical feedstock. Conversion of biomass to energy is undertaken using two main process technologies: thermo-chemical and bio-chemical/biological. Mechanical extraction and chemical esterification is the third technology for producing energy from biomass, e.g., rapeseed methyl ester (RME) bio-diesel. Within thermo-chemical conversion four process options are available: combustion, pyrolysis, gasification and liquefaction. Bio-chemical conversion encompasses two process options: digestion (production of biogas, a mixture of mainly methane and carbon dioxide) and fermentation (production of ethanol) (McKendry, 2002). Thermochemical conversion of biomass frequently results in multiple and often complex products, even in the presence of inorganic catalysts to improve the product quality (Bridgwater, 2012). In general, biomass conversion can be achieved by three main routes: chemical, biochemical and thermochemical route (Basu, 2010). An overview is shown in Figure 1.2.

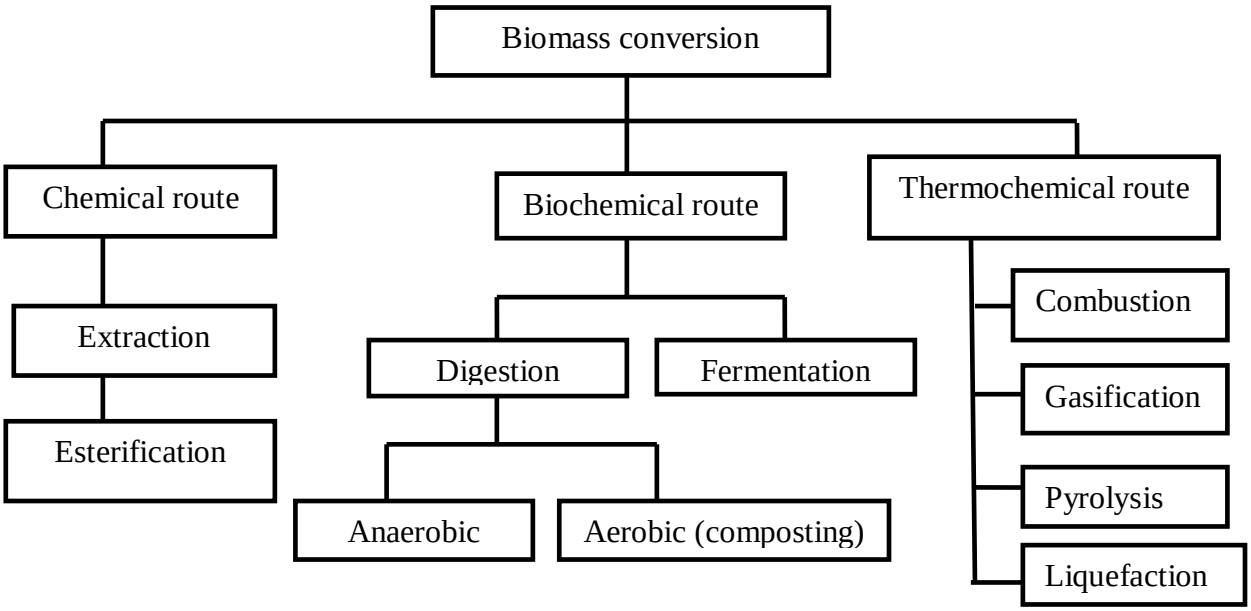


Fig. 1.2 Three main routes of biomass conversion into renewable fuels and/or added-value products (Basu, 2010).

Methods of coffee waste management are outlined to create awareness of the opportunities and constraints associated with the maximization of coffee by-product utilization and the reduction of environmental pollution. The application of environmentally sound disposal methods requires an understanding of the range of waste utilization, treatment and recycling options. Traditionally, coffee pulp and husk have found only limited applications as fertilizer, livestock feed, compost, etc. These applications utilized only a fraction of available quantity and the methods were not technically very efficient (Murthy and Naidu, 2012). Thus, there is a crucial need to counterpart this production with proper utilization and industrial application of coffee by-products.

Factors that influence the choice of the conversion process are the type and quantity of biomass feedstock; the desired form of the energy, i.e., end-user requirements; environmental standards; economic conditions; and project specific factors (McKendry, 2002). Several attempts have been made to re-use the coffee processing solid residues, which include direct use as fuel in farms, animal feed, fermentation studies, adsorption studies, biodiesel production, briquetting, pelletizing, tannin extraction and production of specialty commodities (Echeverria and Nuti,

2017). Coffee processing by-products can be converted through thermochemical or biochemical processes into biogas, biofuel, biodiesel, bioethanol or could be directly subjected to combustion. A pretreatment technique such as drying and torrefaction could be applied in the case of high humidity content in order to remove water from the coffee processing by-products. Moisture harms the performance of the thermochemical process and influences the quality of gas produced. Removing moisture increases the energy value of the coffee by-product.

The use of coffee processing by-products has also received much attention for environmental applications. In particular, the use of raw and modified coffee residues for the removal of pollutants from aqueous and gaseous phases is addressed. The modification of coffee residues includes chars, activated carbon, and catalyst support production. Raw coffee processing residues and their corresponding chars can be used as biosorbents for the removal of heavy metals and organic dyes from aqueous solution. Furthermore, the chars can be transformed into activated carbons through different activation protocols. These activated carbons could be applied efficiently for the removal of pollutants from aqueous and gaseous effluents. Moreover, these activated carbons can be used as a catalyst support for the elimination of several organic compounds. Because of its environmental benefits, bioethanol is regarded as a promising biofuel substitute for gasoline in the transportation sector. However, to make it competitive with fossil fuels, it is necessary to reduce production costs by using new, alternative biomass feedstock (Franca et al., 2009).

Pyrolysis of biomass is regarded as a promising technology for using the renewable biomass resources, through which biomass can be thermally converted into liquid pyrolytic oil (i.e., bio-oil), fuel gas, and solid biochar (Bridgwater and Peacocke, 2000; Abdullah and Wu, 2011; Burton and Wu, 2012). The pyrolysis process can be generally classified into three types: conventional, fast and flash, depending upon the operating conditions employed in the process, such as time, temperature and heating rate (Demirbas and Arin, 2002; Mohan et al., 2006).

Conventional pyrolysis involves decomposition at a low heating rate and long retention time to produce biochar. Fast pyrolysis occurs with a very high heating rate over a short retention time, largely for achieving a high yield of biological oils, known as bio-oil. Since bio-oil is

appealing as an alternative to depleted fossil-based fuels, fast pyrolysis is receiving increasing attention (Ngo et al., 2015). In conventional pyrolysis, a high yield of hydrogen-rich gas is obtained working at high temperature and for a long residence time (Iwasaki, 2003; Li et al., 2004), whereas char production is increased by using low temperature and a low heating rate (Savova et al., 2001). Another possible pyrolysis alternative, called flash or fast pyrolysis has been applied to maximize the yield of liquid. In this case, a very high heating rate, low residence time and temperatures of around 500 ^{0}C are used (Acikgoz et al., 2004; Tsai et al., 2006). The detailed review conducted by Jahirul et al. (2012) reports that the relative distribution of products is dependent on pyrolysis type and pyrolysis operating parameters, as shown in Table 1.1.

Table 1.1. Typical operating parameters and products for pyrolysis process

Pyrolysis process	**Solid residence time (s)**	**Heating rate (K/s)**	**Particle size (mm)**	**Temp (K)**	**Product yield (%)**		
					Oil	**Char**	**Gas**
Slow	450-550	0.1-1	5-50	550-950	30	35	35
Fast	0.5-10	10-200	<1	850-1250	50	20	30
Flash	< 0.5	>1000	<0.2	1050-1300	75	12	13

Source: Jahirul et al. (2012)

The treatment of coffee by-products through oxygen-driven biological methods, such as composting, would serve a dual purpose, i.e., fertilizer production and environmental protection (Murthy and Naidu, 2012). Indeed, composting has become one of the most widely-known and accepted technologies for the recycling of agricultural waste materials under aerobic conditions. It transforms waste materials into high quality amendment/fertilizer, rich in organic matter and nutrients (Insam and De Bertoldi, 2007).

1.5 Membrane process technologies

1.5.1 Fundamentals of pervaporation

Pervaporation is a membrane separation technique in which a liquid mixture is partially vaporized during transport through a dense (molecularly porous) membrane by using a vacuum at the permeate side of the membrane (Baker, 2004). A schematic representation of the pervaporation process is given in figure 1.3. The phase transition that occurs during pervaporation is different in comparison to other membrane processes. The transport mechanism in pervaporation involves three major steps, i.e.: (i) sorption of components into the membrane at the feed side, (ii) diffusion through the membrane and (iii) desorption of components at the permeate side. The separation mechanism is based on the difference in solubility of components into the membrane structure and different diffusion rates through the membrane material (Chovau, 2013).

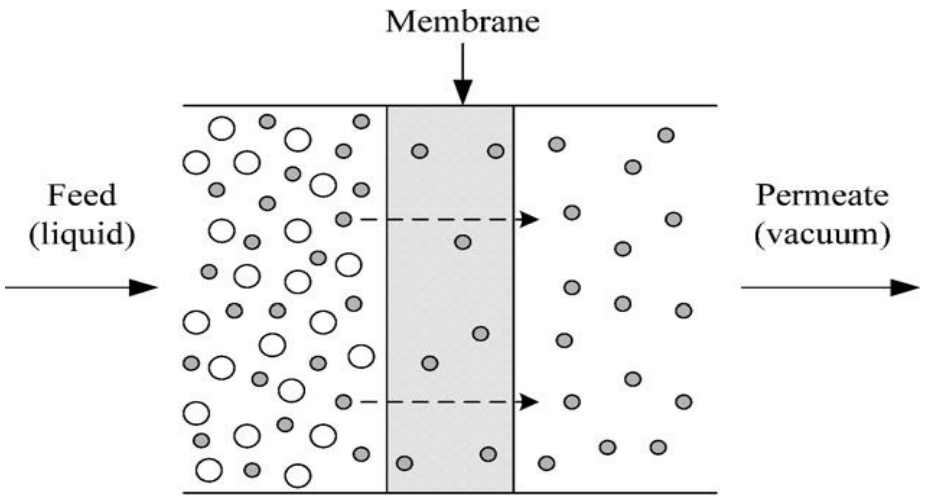


Figure 1.3: Schematic representation of the pervaporation process

Separation of liquid mixtures by partial vaporization through a membrane (nonporous or porous) is the separation principle in pervaporation. This results in the collection of permeating components in vapor form, which may be either removed by flowing an inert medium or by applying a vacuum on the permeate side. The driving force for pervaporation is the difference in

chemical potential, corresponding to the concentration gradient between phases on the opposite sides of the interfacial barrier (Jyoti et al., 2015). In the last two decades, pervaporation is finding a wide range of application areas such as separation of liquid hydrocarbons (petrochemical application, alcohol/ether separations) (Aouinti et al., 2015; Ribeiro et al., 2012; Li et al., 2011), removal of volatile organic compounds (VOCs) from water (Kujawa et al., 2015; Ghoreyshi et al., 2014), removal of water from glycerin (Mah et al., 2014), and dehydration to intensify esterification reactions (Delgado et al., 2009; Zhu et al.,2013).

Pervaporation is a type of membrane separation process with a wide range of uses such as solvent dehydration and separation of organic mixtures. It has significant advantages in azeotropic systems where traditional distillation is only able to recover pure solvents with the use of entrainers, which then must be removed using an additional separation step. Pervaporation can be used to break this azeotrope, as its mechanism of separation is very different to that of distillation. In theory pervaporation can be used to separate any liquid mixtures but in practice, pervaporation tends to be used to separate azeotropic mixtures, close boiling-point mixtures, for the recovery of small quantities of impurities and for the enhancement of equilibrium reactions (Chapman et al., 2008). Membrane process technologies are claimed to be sustainable alternatives to classical separation technologies. Only a part of the feed is vaporized in this way and hence an energy reduction can be achieved in comparison to distillation (Chovau, 2013).

Pervaporation can be integrated with either distillation or a chemical production step to provide intensification and energy integration. A pervaporation-distillation hybrid system leads to a clean technology and offers potential savings in energy because of the reduced thermal and pressure requirements. The separation feature is based on affinity with membrane materials; the molecule having a higher affinity is sorbed and diffuses through the membrane while the membrane retains molecules having a low affinity (Jyoti et al., 2015).

1.6 Research gap

The overall research gap and the major focus areas of the present study are as follows:

The few existing case studies addressing wet coffee processing industries (Endris et al., 2008; Haddis and Devi, 2008; Beyene et al., 2012) indicate that disposing untreated coffee wastewater into local water bodies results in the pollution of downstream water sources, and people residing in the vicinity of the wet coffee processing plants suffer from different types of diseases. However, there have been no detailed studies evaluating the impact of coffee wastewater effluents on the organic load, nutrient enrichment and eutrophication of the nearby water bodies. Therefore, the second chapter presents an assessment of effluent quality and the magnitude of impact on the downstream water quality.

Several recent studies indicate that coffee byproducts (husk, pulp, and spent coffee) can be suitable for bioethanol production using fermentation technology (Gouvea et al., 2009; Ayele, 2011; Shenoy et al., 2011; Choi et al., 2012; Woldesenbet et al., 2016). However, no research has been carried out to compare different coffee waste fractions as potential substrates, using both baker's yeast and lignocellulosic yeast GSE16-T18 (C5) for fermentation followed by purification of the produced bioethanol via pervaporation. Thus, the third chapter focuses on both bioethanol production and its quality upgrading by pervaporating the produced bioethanol using alcohol selective membranes.

The environmental and health problems caused by coffee pulp have been addressed in some studies (Haddis and Devi, 2008; Ayele, 2011; Beyene et al., 2012; Woldesenbet et al., 2014). However, no research has been carried out to investigate the potential of the dried coffee pulp for bioethanol fermentation using the lignocellulosic yeast GSE16-T18 and its purification by pervaporation. Thus, the current study focuses on bioethanol production from dried coffee pulp and its quality upgrading by pervaporating the produced bioethanol using an alcohol selective membrane. Hydrophobic membranes must be used to recover organic compounds from aqueous solutions by pervaporation (Rozicka et al., 2014). In this study, the use of different concentrations of diluted sulfuric acid pretreatments was evaluated by varying the mixing ratio of solid to liquid with the aim of producing hydrolysates for bioethanol production from dried coffee pulp. For the fermentation of the hydrolyzed samples, two different types of yeasts (baker's yeast and lignocellulosic yeast) were used. An alcohol selective polyvinyl alcohol pervaporation membrane was used for pervaporating the fermented broths. Besides, a simulation

of pervaporation units (both hydrophobic and hydrophilic) to estimate their long-term potential as alternative separation systems was performed using Aspen Plus. Furthermore, a comparison of the performance of real membranes used in other studies in terms of their energy requirement was made. The details are explained in Chapter 4.

Recent case studies (Franca et al., 2009; Kassa et al., 2011; De Rezende et al., 2012; Shemekite et al., 2014; Degefe et al., 2016) reported composting of coffee husk with cow dung, fruits/vegetables, effective microorganisms and Khat (*Catha edulis*). However, no research was carried out to investigate the composting and co-composting of coffee husk and pulp with source separated municipal solid waste including the leaves of false banana *(Ensete ventricosum)*, fruits, vegetables, khat/*Catha edulis*, and soft dry wood at different proportions. This was carried out in the current study, with an analysis of heavy metal concentrations of matured compost samples, and seed germination and growth tests on composted samples. Further biochar application on composted samples was studied to verify the productivity/yield of the fresh head weight of the cabbage. Compost was produced from coffee husk and pulp independently, and by mixing it in various proportions (0, 33, and 50 %) with degradable organic municipal solid waste. To study the maturity of the produced compost, the seeds of cabbage were grown on the composted samples. Furthermore, the concentrations of heavy metals of the matured compost samples were analyzed and compared with compost guidelines/standards of different countries. Finally, to check the maturity and yield/productivity of the produced compost samples, various proportions of each composted sample (0, 25, 50, 75, 100%) with local soil and as well as with biochar prepared from different fractions of coffee byproducts (as indicated in Chapter 6) were used to verify the fresh head weight yield of the cabbage. The details are explained in Chapter 5.

Pyrolysis of biomass is suggested as an alternative technology for using renewable biomass resources, through which biomass can be thermally converted into liquid pyrolytic oil (i.e., bio-oil), fuel gas, and solid biochar (Abdullah and Wu, 2011). Even though there are few studies on the pyrolysis of coffee husk and spent (ground) coffee, no comprehensive study was conducted on the pyrolysis of the different fractions of coffee waste (coffee husk, pulp, parchment, silver skin and spent coffee ground). Thus, the pyrolysis study was conducted to describe the thermogravimetric analysis of the different coffee byproducts, to evaluate the overall yield of

biochar, bio-oil and bio-gas produced by using a non-catalytic thermal processes, semi-quantitative elemental analysis (XRF), thermal desorption gas chromatography–mass spectrometry (GC/MS) and pyrolysis gas chromatography–mass spectrometry (GC/MS) after desorption and activation of the produced biochar samples were performed. The details are explained in Chapter 6.

1.7 Scope

The overall scope of the thesis is to study the resource recovery potential of different coffee waste fractions in view of sustainable coffee production via biomass conversion technologies such as hydrolysis, fermentation, pervaporation, composting and pyrolysis. Besides, the impact of wet coffee processing industries on the environment will also be investigated. In order to reach this target, aspects of different areas must be taken into consideration.

A major part of this study is dedicated to the understanding of the overall bioethanol, bio-oil, biogas, biochar, activated carbon and quality compost production from coffee waste fractions. The wet coffee processing wastewater itself will also be discussed in detail. Finally, the produced biochar will also be investigated on cabbage seed productivity yield with the compost samples produced from composting and co-composting of coffee pulp and husk.

The main topics addressed in this dissertation are:

- Assessment of the effluent quality of wet coffee processing wastewater and its influence on downstream water quality;
- Valorization of coffee byproducts for bioethanol production using lignocellulosic yeast fermentation and pervaporation;
- Production of bioethanol by pervaporation of the fermentation broth of dried coffee pulp;
- Composting and co-composting of coffee husk and pulp with source separated municipal solid waste; and
- Valorization of coffee processing byproducts through pyrolysis.

1.8 Research objectives

The overall objective of the thesis is:

- to evaluate the impact of wastewater coming from wet coffee processing industries;
- to assess the feasibility of coffee waste fractions for production of bioethanol, biochar, bio-oil, activated carbon and compost;
- to determine the potential of bioethanol production from coffee waste fractions.

1.9 Thesis outline

An outline of the content of the thesis with a description of its seven chapters is provided below.

Chapter 1. This introductory chapter sets the scene for the Ph.D research. A short historical overview of coffee brewing is provided after which the current challenges of coffee production are introduced. These challenges are then translated into the research objectives of this thesis of which the structure (in seven chapters) is outlined.

Chapter 2. This chapter focuses on the assessment of the effluent quality of wet coffee processing industries wastewater and its influence on surface water quality and consists of three sub-sections. In the first part, the general physicochemical characteristics of the upstream water and downstream is discussed. In the second part, the state of organic load and dissolved oxygen is described. In the third part, nutrient enrichment and eutrophication status of upstream, effluent, and downstream water bodies are discussed. Finally, a conclusion of the chapter is provided with a focus on finding an economical and easily adaptable technology for the treatment of wastewater derived from coffee production.

Chapter 3. The valorization of coffee byproducts for bioethanol production using lignocellulosic yeast fermentation and pervaporation is evaluated. For this purpose, the study includes the most prominent coffee waste fractions. These are parchment, husk, defected coffee beans, silver skin

and spent coffee ground. These fractions are produced when washed coffee is dried and deshelled, coffee berries are processed by the dry method, immature or overripe coffee bean, which is too low in quality is separated, coffee is roasted, and as a residue of coffee brewing, respectively. For the determination of the optimum bioethanol yield, all five coffee waste samples (husk, silver skin, defected coffee bean, spent coffee, parchment) and their mixture were acid hydrolyzed with 3% (v/v) H_2SO_4 (99%, Sigma Aldrich) or distilled water and autoclaved (1 bar pressure, 121 ºC for 20 min) in a SystecV-150 autoclave (Systec, Germany). After the hydrolysis, samples were centrifuged and the supernatant was filtered using a 0.2 µm filter. To verify the impact of the duration of autoclaving on the reducing sugar concentration, all samples hydrolyzed with 3% H_2SO_4 were autoclaved once and twice. The samples were then filtered and analyzed.

Ethanol and sugar concentrations were measured with HPLC. The slurry was neutralized and the pH adjusted to 6 using pure pellets of KOH (VWR International, United States). The neutralized material was saccharified using 5% w/w (total solid) of cellulases from *Trichoderma reesei* ATCC26921 (NS50013, Novozymes, Denmark) and 0.5% w/w (total solid) of β-glucosidases from *Aspergillus niger* (C6105, Novozymes, Denmark).

Chapter 4. This chapter evaluates the potential of the dried coffee pulp for bioethanol production and upgrading the quality of the produced ethanol by using a pervaporation membrane. First of all, coffee pulp was ground and pretreated with different concentrations of diluted H_2SO_4 (0, 1, 2, 3, 4, 5 and 10 vol %) at different solid: liquid ratios (1:1, 1:2, and 1:4). Afterwards, the neutralized hydrolysate was fermented using *S. cerevisiae* and lignocellulosic yeast GSE16-T18 strain. Before fermentation of the hydrolysate with the lignocellulosic yeast, the enzyme accellerase was used for hydrolysis. Finally, the results of the fermented feed solution which is filtered and pervaporated at different temperatures (30, 40, 50 and 60 °C) using the PolyAn POL_AL_M1 pervaporation membrane is discussed.

Chapter 5. In this chapter composting and co-composting of coffee husk and pulp with source separated municipal solid waste (SSMSW): a breakthrough in valorization of coffee waste is investigated. Coffee husk and pulp were mixed independently with SSMSW in different

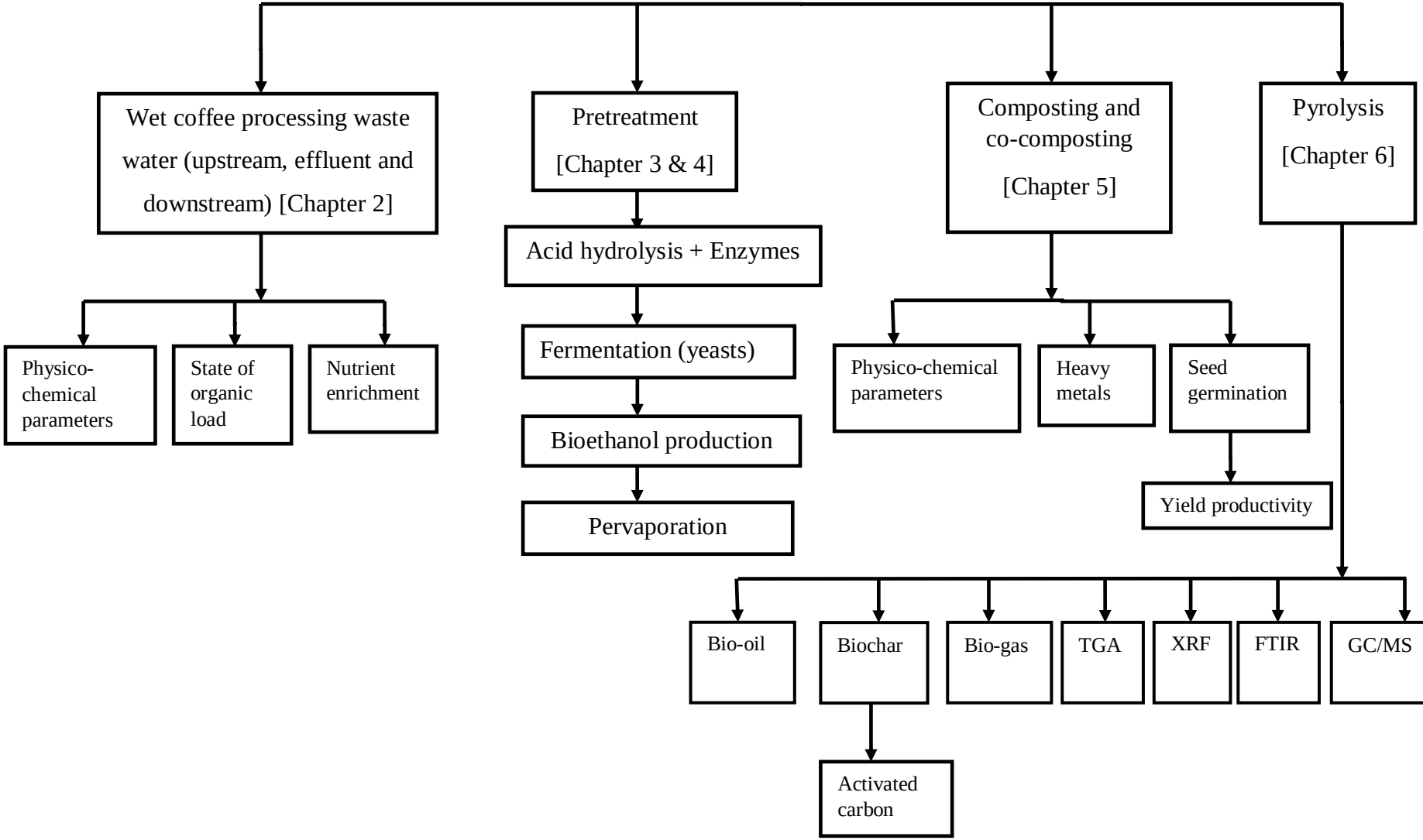
proportions (0, 33, 50 and 100%), and composted in triplicates with a total of 24 composting piles for 3 months. The aerobic windrow composting method was applied. From each compost type different physicochemical parameters (pH, electrical conductivity, organic carbon, organic matter, total nitrogen, available phosphorous, carbon to nitrogen ratio, and heavy metals content) were analyzed. Finally, the seed germination, growth, and fresh head weight yield of each compost type were investigated on each matured compost type using cabbage seed (*Brassica oleracea)* and the results are discussed.

Chapter 6. The present study investigates the valorization of coffee processing byproducts through pyrolysis. For this purpose, the pyrolysis of five different coffee waste fractions (coffee husk, pulp, silver skin, parchment and spent coffee) using non-catalytic processes was considered. Thermogravimetric analysis (TGA) was performed for all samples (coffee husk, pulp, silver skin, parchment and spent coffee) in a nitrogen atmosphere and in a temperature range up to 550 °C (20 °C/min). After an isothermal period, the atmosphere was changed to O_2 and heating was continued to 900 °C (20 °C/min). The pyrolysis process using the low temperature conversion conditions was applied in the samples and produced three fractions: pyrolysis bio-oil, pyrolytic bio-char, and bio-gas fractions. Finally, activated carbon was prepared from each of coffee waste fractions using quartz tube reactor. In general, the biochar, bio-oil, biogas and activated carbon yield of each coffee waste fraction were compared and discussed in detail.

Chapter 7. The general conclusions of the study are described in this part. In addition, recommendations for further research for sustainable coffee production options are given.

A schematic overview of the thesis is indicated below.

2.0 Schematic overview of the thesis



2. Assessment of the effluent quality of wet coffee processing wastewater and its influence on downstream water quality

Abstract

The previous chapter introduces the overall scope and contents of the entire manuscript thesis. The objective of this chapter was to evaluate the impact of effluents from traditional wet coffee processing plants on the downstream water quality in Ethiopia. Samples were collected from 11 rivers/streams associated with wet coffee processing plants. Effluent quality parameters for these plants were measured before intake, during processing and after effluent discharge. Composite wastewater samples were collected at the peak hours of coffee processing. Acidic pH values were recorded in all plant effluents. The organic content of the effluent varies from one plant to the other and it was considerably high, with maximum values of 7200 mg/L and 871 mg/L for COD and BOD_5, respectively. This high level of organic content in the effluent depleted oxygen to the level of 0.25 mg/L. The organic load and the presence of nutrients (particularly phosphates and nitrates) invoke a large risk for eutrophication. The results revealed that the variation in soaking time of coffee beans, fermentation of the coffee pulp, and absence of appropriate treatment facilities were the major factors associated with the magnitude of the water pollutant parameters released by the coffee processing plants. In general, the measured values of effluent parameters significantly deviate from both the Ethiopian-EPA and US-EPA guidelines. Thus, water bodies and ecosystems located downstream of the traditional wet coffee processing plants are at an alarming risk of ecological disruption. In addition, there might be also severe health consequences on the nearby residents. This calls for further research in the design and implementation of coffee waste valorization and treatment in view of sustainable coffee production.

Keywords: Wet coffee processing; wastewater discharge; environmental pollution; sustainable production

2.1 Introduction

According to United States Department of Agriculture data (USDA, 2011), the global coffee production in 2010/2011 is estimated to be above 8.2 million tons. Over 2.25 billion cups of coffee are consumed every day globally. Over 90% of coffee production takes place in developing countries, whereas consumption is mainly in the industrialized economies (Ponte, 2002).

Ethiopia is the origin of highland coffee (*Coffea arabica* Linnaeus), a plant earlier known as *Jasminum arabicum laurifolia* Jussieu. This coffee tree species, the only native coffee in the world, has traditionally been tended and harvested as a wild tree in the highland forests of southwestern Ethiopia (Schmitt, 2006), mostly in the former Kaffa Province. In Ethiopia, coffee plays a central role in the incomes of more than one million coffee-growing households and the livelihood of over 15 million people directly or indirectly depends on this commodity crop (LMC, 2000). According to data of the Ministry of Agriculture and Rural Development (MoARD) of Ethiopia for 2013, there were 1722 coffee processing (wet and dry) plants in Ethiopia, owned by private persons, cooperatives, and the government. Furthermore, according to data from the Ethiopian coffee and tea development and marketing authority for 2016/17, the total number of coffee processing plants in Ethiopia has now surged to 2156 (ECTA, 2017) (Table 2.1).

Table 2.1 National wet and dry coffee processing industries (June 2017)

Region	**Wet coffee processing**				**Dry coffee processing**				**Grand**
	Privately owned	**Association**	**State farm**	**Sub-total**	**Privately owned**	**Association**	**State farm**	**Sub-total**	**Total**
Oromia	367	165	15	547	604	58	6	668	1215
SNNP	520	175	-	695	181	44	-	225	920
Gambela	7	-	-	7	14	-	-	14	21
Total	894	340	15	1249	799	102	6	907	2156

Source: ECTA, 2017

Almost all wet coffee processing plants in Ethiopia are located close to water bodies. This is because a lot of water (10-20 liters of water/kg of coffee bean) is needed for washing the beans, removing the pulp and the mucilage, but also in order to use the water bodies for direct disposal of the wastewater released from the wet coffee processing plants. All in all, wet coffee processing industries in Ethiopia are not re-using the water, which is once used for depulping and fermentation. Thus, all the generated wastewater is directly released to downstream water bodies, and sometimes in disposal pits. While there are some wet coffee processing plants that use disposal pits to stabilize the generated wastewater, these disposal pits are constructed without following the correct design and dimensions. In addition, they lack the proper linings (HDPE or cemented floor, for example) to protect against leakage of the effluents into the underground water and the holding capacity of the disposal pits is not taken into consideration during construction. Thus, the coffee processing water and its wastewater are routinely discharged into nearby streams and rivers.

Fig. 2.1. Disposal pits used by wet coffee processing plants: D and F

Figure 2.1 illustrates disposal pits used by wet coffee processing plants. In this regard, proclamation number 602/2008 (FDRE, 2008b) and the Council of Ministers Regulation number 159/2008 (FDRE, 2008a) of Ethiopia proclaimed that coffee processors shall dispose of waste without causing harm to the environment, the public or individuals. However, in most cases, there is a lack of continuous follow-up and implementation. Industrial processing of coffee cherries for both dry and wet processes is outlined in Figure 2.2.

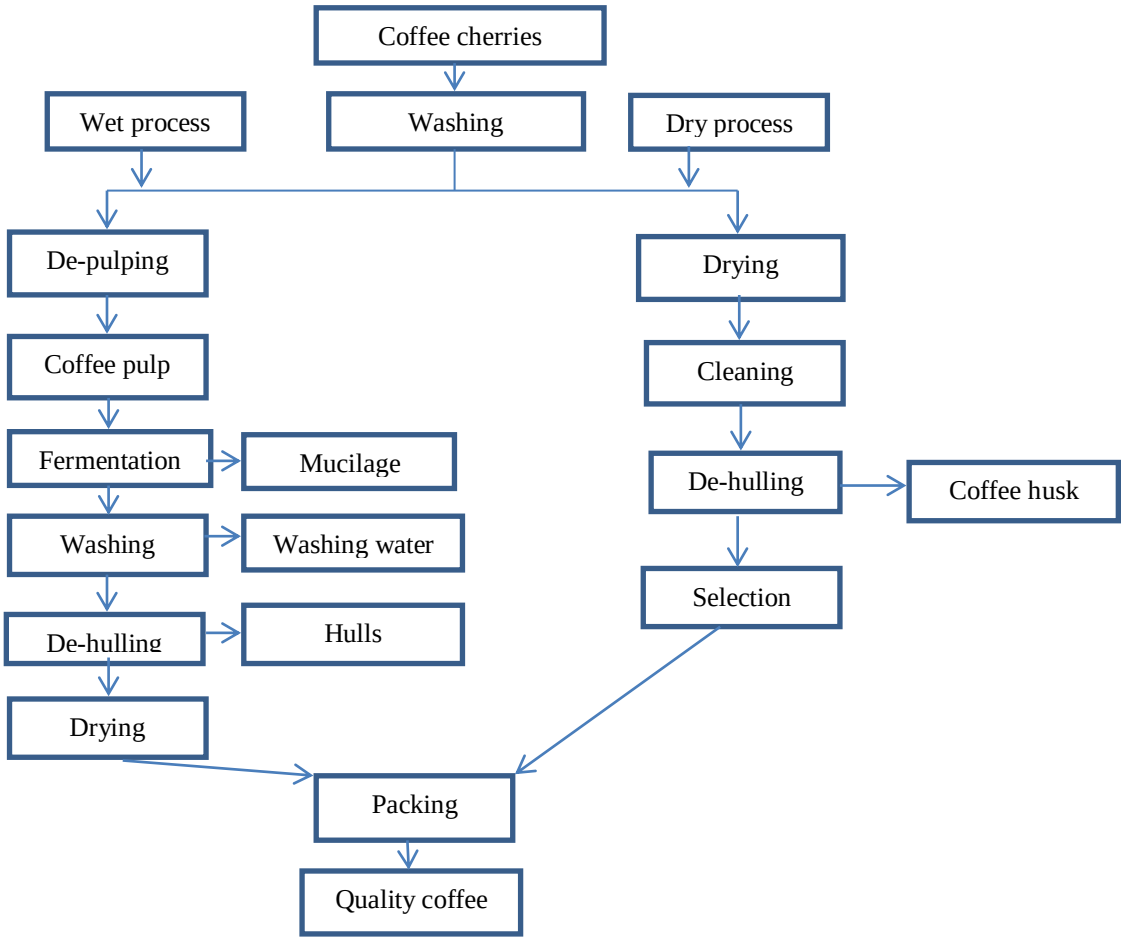


Fig. 2.2 Industrial processing of coffee cherries [Modified from Pandey et al. (2000a)]

The wet coffee processing procedure requires mechanical removal of pulp with the help of water, as a result of which it produces a considerable volume of wastewater. In wet industrial processes, a large amount of coffee-pulp (about 29% dry weight of the whole coffee berry) is produced as the first byproduct (Corro et al., 2013). It is obtained during the wet processing of

coffee and for every 2 tons of coffee processed, 1 ton of coffee pulp is generated, whereas in the dry process 0.18 ton coffee husk is generated for every ton of fresh coffee cherries (Adams and Dougan, 1981).

Most of the coffee processing plants in Ethiopia prefer to follow the wet processing method because wet processed coffee is considered superior in quality to dry processed coffee. In addition, it obtains higher prices and has a better aroma/flavor than the coffee obtained by the dry processing method. However, wet coffee processing plants discharge untreated effluents into the nearby water bodies and open land. In addition, water consumption is high for this method. In this regard, Kivaisi et al. (2010) estimated that coffee processing is generating about 9 million m^3 of wastewater, and 600,000 tons of husks annually in the East Africa region. Similarly, Devi et al. (2008) indicated that the wastewater generated from coffee processing has high concentrations of organic pollutants like pectin, proteins, and sugars. Due to the high pollutant content, its disposal without treatment in water bodies has become undesirable due to the danger this poses to the water bodies and to human health.

Therefore, in this chapter, an assessment of effluent quality and the magnitude of impact on the downstream water quality, is described in detail to answer the research gap, which is indicated in section 1.6 of chapter 1.

2.2 Materials and methods

2.2.1 Study area

The study was conducted in the Jimma zone, Oromiya region, Ethiopia. From the 18 districts of the Jimma zone, the Limmu Kossa, Manna and Gomma districts were selected because these are the three leading districts in terms of wet coffee processing. For the data collection, 2, 3 and 6 wet coffee processing plants were selected from the Limmu Kossa, Manna, and Gomma districts, respectively, because of their proximity to water sources. For simplicity letters from A-K are used as codes throughout this chapter. Of these 11 wet coffee processing plants, only plants D and F have temporary disposal pits to stabilize the effluent, whereas all the other plants

discharge their effluent without any form of treatment. Figure 2.3 shows the area of study and the sampling points.

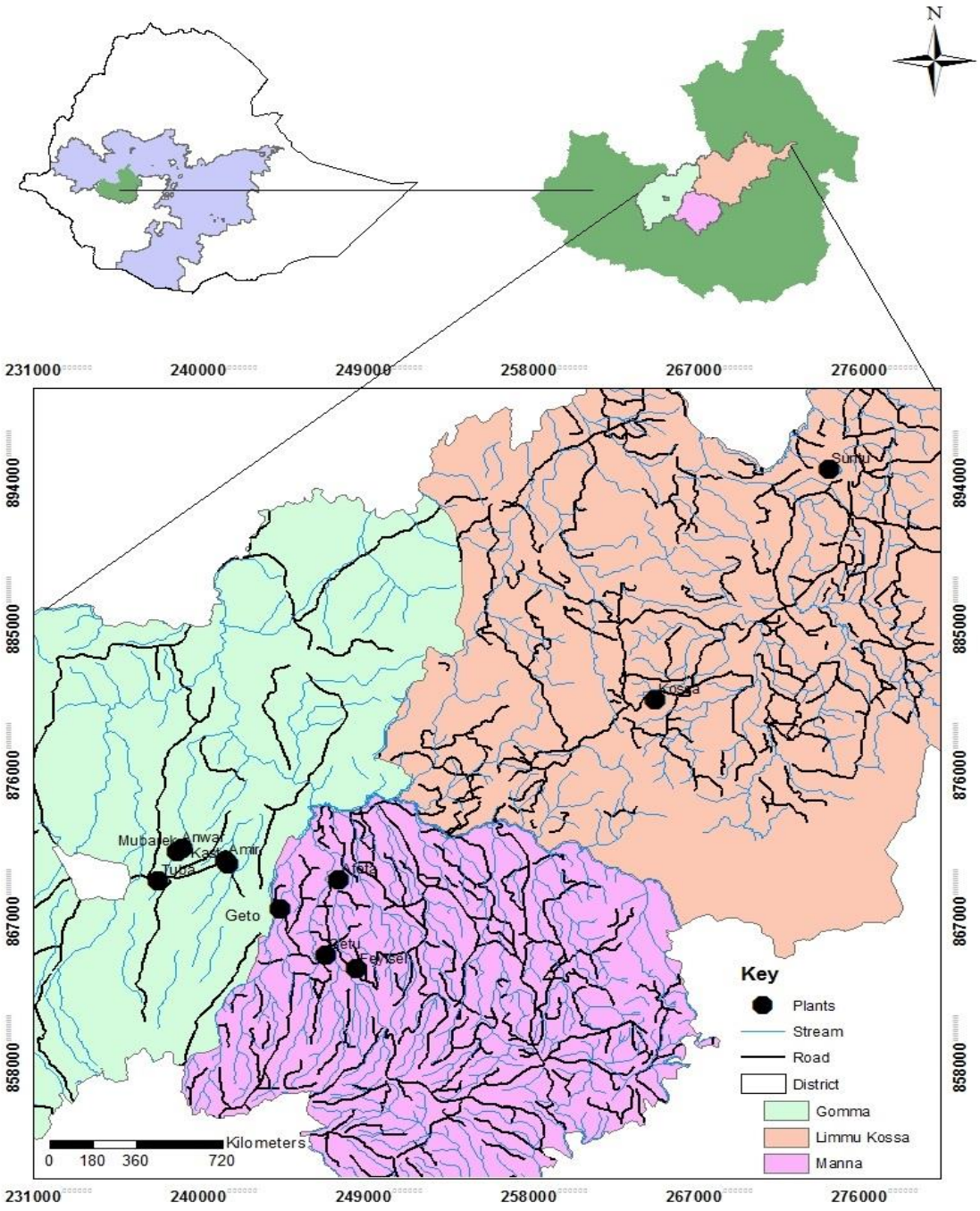


Fig. 2.3 Study area and sampling points

2.2.2 Sampling

Since wet coffee processing is a seasonal activity, the study was conducted during the harvesting period for ripe coffee cherries, which varies from year to year and usually falls between October and January. To study the impact of these coffee processing industries on downstream water bodies, water samples were taken from the upstream inlet water (water used for washing, depulping, fermenting), from the effluent wastewater after the depulping of the coffee beans (removing the pulp and mucilage), and from the nearest downstream water bodies, that is, after the effluent is discharged into the nearby river water. However, samples could not be taken in the downstream water bodies in two coffee plants (downstream site of plants G and I) due to road inaccessibility. As a result, a total of 31 sites were sampled (all 3 sampling sites for 9 plants, plus two sites for a further two plants).

To ensure that the sampling was representative, composite samples of the wastewater released by the plants were collected at the peak hours of coffee processing. In addition, composite water samples were also taken from upstream and downstream rivers/streams. All samples were collected using clean polyethylene plastic bottles that were thoroughly washed with deionized water. The water samples were filtered onsite before the analysis of NO_3-N, NH_4^+-N, TN (Total nitrogen), and phosphorous as ortho-phosphate. Then, the samples were properly and carefully labeled, sealed and transported to the laboratory of the Department of Environmental Health Sciences and Technology, Jimma University, Ethiopia. Cold storage was maintained throughout the process until analysis was performed. Every sample was taken in triplicate and the average results were reported.

2.2.3 Water and wastewater analysis

On-site measurements of samples from the upstream and downstream river water and samples from wastewater for electrical conductivity (EC), pH, temperature and dissolved oxygen (DO) were carried out using a Hach multi-meter probe (P/N HQ40d multimeter). To measure total suspended solids (TSS) and BOD_5, a gravimetric method (by using glass microfiber GF/A

Whatman filter paper having 4.7 cm diameter and with a pore size of 1.6 micron) and the Azide modification of the Winkler method (by using aerator TRITON 2000cc, China) were used, respectively. For the remaining parameters (COD, NO_3-N, NH_4^+-N, TN, and phosphorous as ortho-phosphate), LCK test kits (Hach Lange, Germany) were used.

2.3 Discussion of results

2.3.1 General physicochemical characteristics of the upstream water and downstream

The pH, EC, temperature and TSS measured at the selected sampling points are presented in Table 2.2.

Table 2.2 Average results of the general physico-chemical parameters (pH, EC, temperature and TSS) measured from upstream, from the influent and from the downstream water bodies of wet coffee processing plants.

Wet coffee processing plant	**Sampling site**	**Physico-chemical parameters**			
		pH	**EC (µS/cm)**	**Temp (°C)**	**TSS (mg/L)**
A	Upstream	6.6	105	21.7	84
	Effluent	5.2	102	20.7	66
	Downstream	6.9	104	19.3	96
B	Upstream	6.0	87	19.3	38
	Effluent	6.0	98	18.8	38
	Downstream	6.3	86	17.8	46
C	Upstream	5.1	122	17.4	8
	Effluent	5.1	201	21.0	92
	Downstream	5.1	143	17.2	22
D	Upstream	6.3	69	19.5	48
	Effluent	4.5	3270	19.1	780
	Downstream	6.6	135	19.9	10

E	Upstream	6.0	63	19.0	36
	Effluent	5.6	104	20.3	44
	Downstream	6.0	92	18.7	60
F	Upstream	5.7	72	21.2	38
	Effluent	4.2	777	21.6	2260
	Downstream	5.9	125	19.1	48
G	Upstream	7.4	101	20.5	18
	Effluent	6.8	112	20.9	50
	Downstream	ND	ND	ND	ND
H	Upstream	6.6	135	19.7	4
	Effluent	5.4	292	18.9	88
	Downstream	5.5	172	20.8	40
I	Upstream	6.8	105	22.3	158
	Effluent	4.8	3700	23.9	1440
	Downstream	ND	ND	ND	ND
J	Upstream	7.2	81	20.4	68
	Effluent	5.4	295	21.8	84
	Downstream	4.3	600	24.1	62
K	Upstream	6.6	93	19.3	6
	Effluent	3.6	1134	18.7	1240
	Downstream	4.4	871	21.7	72

*ND = Not detected

The pH is generally lower in the effluent. In all cases, the pH is below 7, which indicates that all the effluents from wet coffee depulping processes lead to acidic conditions, which can be toxic to the downstream ecosystem. It was also observed that the pH of effluents from D, F, I and K plants/factories were measured to be below 5 (Table 2.2). This may be due to the nature (composition and variety) of the coffee bean itself, the harvesting time of the bean, the soaking duration of the depulped coffee bean, the fermentation time to remove the mucilage (the presence/absence of sunlight during fermentation), and differences in processing the coffee bean

(for example the amount of water used for washing and depulping). However, at plant sites A, B, D, and F the downstream pH value is higher than the corresponding upstream value. This might be due to the self-buffering capacity of the receiving water. From the results, it is evident that the pH in the effluent drops to 3.6 (K), indicating the active decomposition of organic matter. This shows that there was fermentation of sugars in the mucilage in the presence of yeasts to alcohol and CO_2. As the organic waste oxidizes, CO_2 is released and increases the acidic characteristics of the water, decreasing the pH value below the range of 6-9 (which is the surface water quality standard for ambient environment in Ethiopia) and 5.5-9.0 (which is the US-EPA Standards for Discharge of Environmental Pollutants to Inland Surface Waters) (Table A1 in appendix).

The sugars contained in the mucilage ferment and the organic and acetic acids from the fermentation of the sugars make the wastewater acidic, a condition in which higher plants and animals can hardly survive (Enden and Calvert, 2002). The acidic nature of wet coffee processing industry wastewater has also been reported elsewhere (Beyene et al., 2012; Kefale et al., 2012; Beyene et al., 2014). The direct effects of pH changes involve alterations in the ionic and osmotic balance of individual organisms, in particular, changes in the rate and type of ion exchange across body surfaces. This requires greater energy expenditure, with subsequent effects such as slow growth and reduced fecundity becoming apparent (EFEPA, 2003). The relative increment of pH in downstream water bodies may be due to the buffering capacity of the receiving water. However, if this situation increases with time, the self-purification capacity of these water bodies will decline. In general, the wastewater of wet coffee processing plants has impacted the pH of downstream water bodies. For example, comparison of the upstream and downstream pH values clearly shows that the pH values were measured to be much lower at the downstream sites for plants H, I, J and K.

The electrical conductivity (EC) can be regarded as a crude indicator of water quality for many purposes since it is related to the sum of all ionized solutes or total dissolved solids (TDS) content. The electrical conductivity of the water depends on the water temperature: the higher the temperature, the higher the electrical conductivity. The trend of EC is not uniform, but generally the EC values in the effluent are higher than for the upstream and downstream river sites. The values are in the range from 63.2 µS/cm to 871µS/cm (Table 2.2). The EC concentration of the effluent from plant/factory I (3,700 µS/cm), D (3,270 µS/cm), and K (1,134 µS/cm) plants were

observed to be higher than the other facilities. This value is above the Ethiopian surface water quality standard, which is 1,000 µS/cm (Table A1 in the appendix). This increment in EC may be due to the solubility/decomposition of compounds during depulping and fermentation of the coffee pulp. Differences in the capacity of the coffee pulping mills may explain the differences between plants. EC values downstream in the water bodies are lower due to dilution with water; however, this dilution may not always be sufficient. This finding is consistent with similar studies done by Endris et al. (2008) and Tekle et al. (2015). Generally, it was found that wet coffee processing wastewater has impacted the EC of downstream water bodies. For example, a comparison of the EC values in the upstream and downstream clearly shows that the EC values were measured to be much higher at the downstream sites of the plants: C, D, E, F, H, J, and K.

Total suspended solids (TSS) give a measure of the turbidity of the water. The EC is related to the ionic content of the sample, which is in turn, a function of the dissolved (ionizable) solids concentration. TSS values were indeed observed to follow approximately the trend of EC. This increment in EC and TSS might be due to the presence of inorganic compounds and floating particles having larger sizes, respectively. The TSS values ranged from 4 to 158 mg/L in upstream and 10 to 96 mg/L in downstream water bodies. Coffee mills F, I, K, and D were found to have the maximum TSS values of 2,260 mg/L, 1,440 mg/L, 1,240 mg/L and 780 mg/L in their effluents, respectively (Table 2.2). This may be due to the difference in soaking time, washing frequency, depulping and duration of fermentation of coffee beans. In addition, this may be due to the difference in the type of pulping machine used by the plants. It is obvious that these values surpass by far the Ethiopian surface water quality standards (50 mg/L), and also the US-EPA standards for discharge of pollutants to inland surface waters (100 mg/L) (Table A1 in the appendix).

TSS levels of 38 mg/L, 2,260 mg/L, and 48 mg/L were measured in the upstream, effluent and downstream site of plant F, respectively. The difference in upstream and downstream is only 10 mg/l, which is not that high, perhaps due to the functioning of the temporary disposal pit used by the plant. The maximum value of TSS in this study is larger (2,260 mg/L) than the maximum values reported by Beyene et al. (2012), which was 970 mg/L for the impacted sites, and by Devi et al. (2008), which was 700 mg/L. However, it is consistent with values found in similar studies carried out by Haddis and Devi (2008) and Tekle et al.

(2015), who reported 2,080 mg/L in the effluent of coffee processing mills and 2,504 mg/L in downstream waters, respectively. This high concentration of solids in suspension may lead to negative impacts in the ecosystem. In turbid waters, light penetration is reduced, leading to a decrease in photosynthesis. The resultant decrease in primary production reduces food availability for aquatic organisms higher up the food chain. Suspended solids may interfere with the feeding mechanisms of filter-feeding organisms and the gill functioning, foraging efficiency (due to visual disturbances) and growth of fish.

Suspended solids that settle out may smother or abrade benthic plants and animals and may result in changes to the nature of the substratum. This may then lead to changes in the structure of the biotic community, through the decline of these organisms and their replacement with organisms which burrow in soft sediments. Sensitive species may be permanently eliminated if the source of the suspended solids is not removed (EFEPA, 2003). In addition, as mentioned by Tekle et al. (2015), suspended solids may affect the use of water for various purposes by exacerbating the dissolved oxygen problem by sedimentation and forming oxygen demanding sludge deposits, which may alter the habitat of aquatic microorganisms. Similarly, as described by Enden and Calvert (2002), the suspended material (especially the digested mucilage) builds a crust on the surface, clogging up waterways and further contributing to anaerobic conditions. These TSS concentrations automatically influence the quality of the receiving water bodies. The elevated TSS levels can be toxic to freshwater animals by causing osmotic stress and affecting the osmo-regulatory capability of the organisms and can give rise to obnoxious odors from the decomposition of organic matter (Tekle et al., 2015).

In general, it was found that wet coffee processing plant wastewater impacted the TSS of downstream water bodies. For example, comparison of the TSS values for upstream and downstream clearly shows that the TSS values were measured to increase in the downstream sites of plants A, B, C, E, F, H, and K.

2.3.2 The state of organic load and dissolved oxygen

The results of the organic load measured in terms of biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD), and the level of dissolved oxygen (DO) from upstream, effluent and downstream sites are shown in Table 2.3.

Table 2.3 Average results of the organic load and dissolved oxygen

Wet coffee processing plant	**Sampling site**	**Chemical parameters**		
		DO (mg/L)	**COD (mg/L)**	**BOD_5 (mg/L)**
A	Upstream	6.92	64	56
	Effluent	6.06	360	291
	Downstream	5.50	83	79
B	Upstream	7.65	126	108
	Effluent	7.01	254	185
	Downstream	7.32	124	84
C	Upstream	6.06	93	71
	Effluent	6.00	538	433
	Downstream	5.80	142	139
D	Upstream	7.16	91	67
	Effluent	0.48	6140	846
	Downstream	5.15	121	118
E	Upstream	7.11	129	126
	Effluent	6.09	142	110
	Downstream	6.80	83	66
F	Upstream	5.76	153	104
	Effluent	0.25	7180	869
	Downstream	1.75	149	100
G	Upstream	6.82	134	100
	Effluent	6.34	148	87

	Downstream	ND	ND	ND
H	Upstream	5.15	174	87
	Effluent	0.43	1253	819
	Downstream	1.50	318	269
I	Upstream	6.40	128	111
	Effluent	0.17	7200	871
	Downstream	ND	ND	ND
J	Upstream	6.91	154	149
	Effluent	5.52	455	370
	Downstream	0.15	636	503
K	Upstream	6.46	104	94
	Effluent	0.30	7200	828
	Downstream	0.27	616	505

*ND = Not detected

The minimum dissolved oxygen concentration measured in the upstream water sources was 5.15 mg/L (plant H). The decrement in DO value might be due to the impact of different agricultural practices around the site. The dissolved oxygen showed a significant decrease in all the coffee processing plants from upstream to downstream, with values going down to 0.15 mg/L. The DO concentrations of the effluents from all the plants were found to be lower than the upstream water source, which indicates that the oxygen is consumed during the decomposition of organic matter. Furthermore, the DO concentration of all the downstream sites is lower than the upstream sites. This implies that the downstream water sources are compromised. In addition, plants J, K, H, and F were found to have a DO concentration of 0.15 mg/L, 0.27 mg/L, 1.5 mg/L and 1.75 mg/L, respectively, at the downstream water source. This value is much below the Ethiopian surface water quality standard, which is a minimum DO of 4-6 mg/L to support aquatic life (Table A1 in appendix), which indicates the severe level of pollution of the rivers at the downstream sites. Typically, it was observed that the DO value depleted up to 0.15 mg/L in the downstream (Table 2.3). Anoxic or hypoxic conditions may be lethal within short time scales (minutes to hours). The sensitivity of many species, especially fish and invertebrates, to changes

in dissolved oxygen concentrations depends on the species and the life stages (eggs, larvae or adult) and behavioral changes (feeding and reproduction) (EFEPA, 2003).

The relative improvement of DO downstream of plants B, D, E, F, and H might be due to the relative stabilization of the wastewater in the disposal pits, self-purification of aquatic systems and dilution of the effluents with downstream water sources. On the other hand, no improvements in DO values were observed downstream of plants A, C, J and K. Thus, self-purification is not sufficient for every plant. In this regard, Cox (2003) reported that self-purification of streams and rivers require both biological and chemical processes. Oxygen is removed from the river water as organic material is oxidized by chemical processes (COD) and the biological activities of aquatic organisms (BOD_5). Sediment or benthic oxygen demand (SOD), which results from organic matter being deposited and incorporated in the channel bed, is another major cause of DO deficiency in rivers (Cox, 2003; Lehman et al., 2004). Consequently, low levels of DO reduce the self-purification capacity of rivers to recover from the waste impact during off season (Beyene et al., 2012). DO concentrations below 5 mg/L may also adversely affect the functioning and survival of biological communities (US-EPA, 1986). Oxygen depletion can cause the death of fish and create dead zones (Lapointe et al., 2000).

Generally, it was found that wet coffee processing plant wastewater impacted the DO content of downstream water bodies. Comparison of upstream and downstream DO values clearly shows that the DO values were measured to be much lower downstream of all the plants.

As can be expected, the chemical oxygen demand (COD) of the effluent is consistently larger than the upstream and downstream values for all mills except the effluent from plant J. This increment of COD and BOD_5 downstream of plant (J) may be due to the impact of a polluted water source joining the effluent of the plant at the downstream side. The increment of COD and BOD_5 in the effluent of the plants is due to the degradation of soluble compounds during the fermentation of the pulp and mucilage. That is, the increment of the values of COD and BOD_5 in the effluents indicated that there is an increment in chemical and biological oxygen demanding waste during fermentation of coffee pulp and mucilage. This indicates that the presence of organic matter consumes the oxygen, which in turn contributes to high COD and BOD_5. It is also evident that the downstream COD value is larger than the upstream value. The effluent COD values of plants I (7,200 mg/L), K (7,200 mg/L), F (7,180 mg/L) and D (6,140

mg/L) were found to be much higher than the other mills. This difference in COD value may occur because of differences in the pulping capacity of the mills, fermentation time to remove the mucilage, and amount of water used in the process (for washing the bean and for fermentation).

Following the trend of COD values, the BOD_5 values are also larger for the effluent than the upstream and downstream values. In addition, as can be seen from Table 2.3, generally the BOD_5 value for downstream is greater than for upstream. In this regard, Enden and Calvert (2002) mentioned that the organic substances diluted in the wastewater break down very slowly by microbial processes, using up oxygen from the water. Due to the decrease in dissolved oxygen content, the demand for oxygen to breakdown organic material in the wastewater exceeds the supply, thus creating anoxic conditions.

According to Woldesenbet et al. (2014), the COD:BOD_5 ratio can be used as an indicator of biological degradability, with ratios below 5:1 indicating a high digestibility. In our case, the ratios of COD:BOD_5 values were below 5:1, which suggests the biological degradability of the coffee waste. Pulp and mucilage consume the oxygen in water, resulting in the death of plants and animals due to the lack of oxygen or the increased acidity (Pandey et al., 2000a). This fact can later result in a proliferation of undesirable microorganisms, bringing foul odors, attracting flies and other insects, and rendering the water undrinkable and useless for many other uses (Navia et al., 2011).

The minimum value of BOD_5 in the effluent and downstream sites of the plants was found to be 87 mg/L and 66 mg/L, respectively, even after stabilization in a pit. Similarly, the minimum value of COD in the effluent and downstream site of the plants was found to be 142 mg/L and 82.5 mg/L, respectively, even after stabilization in a pit (Table 2.3). This indicates that large amounts of chemical and biological oxygen demanding substances in the effluent are released from the coffee processing wastewater into the rivers. If these values are compared with the Ethiopian surface water quality standards, in which the BOD_5 should be below 5 mg/L, and US-EPA standards for surface waters, where the standard is 30 mg/L for BOD_5 and the maximum of 250 mg/L for COD (Table A1 in the appendix), there is a clear indication that these coffee mills are substantially affecting the downstream water source, aquatic life and habitat.

The decrement in BOD_5 and COD values in the downstream water bodies may be due to a reduction of chemical and biological oxygen demanding wastes as the effluents pass through the disposal pits and due to the dilution of river water. For surface water, a BOD_5 above 10 mg/L usually indicates the presence of gross pollution (Nathanson, 2000). In this study, all the effluents and downstream water bodies show values exceeding this limit during the wet coffee processing season. Thus, it was evident that the downstream water bodies were substantially polluted with organic matter. This finding is consistent with other studies (Endris et al., 2008; Beyene et al., 2012; Beyene et al., 2014; Tekle et al., 2015). Haddis and Devi (2008) reported values even as high as 10,800 mg/L BOD_5 and 15,780 mg/L COD for coffee processing effluents.

Comparison of the BOD_5 and COD values we found for upstream and downstream clearly shows that both the BOD_5 and COD values increased in the downstream sites of plants A, C, D, H, J and K. Thus, it can be concluded that the wet coffee processing plants wastewater has impacted the BOD_5 and COD of downstream water bodies.

2.3.3 Nutrient enrichment and eutrophication

Eutrophication is one of the most serious threats to the natural environment resulting from human activity and impact (Chmiel et al., 2009). Table 2.4 shows the values of concentration of nutrients in terms of nitrogen as NO_3-N, NH_4^+-N and TN, and phosphorous as ortho-phosphate.

Table 2.4 Average results of the nutrient enrichment of wet coffee processing plants wastewater at different sites

Wet coffee processing plant	Sampling site	Chemical parameters			
		NO_3-N (mg/L)	NH_4^+-N (mg/L)	TN (mg/L)	PO_4^{3-} (mg/L)
A	Upstream	0.362	0.041	0.72	0.75
	Effluent	1.310	0.594	3.22	0.50
	Downstream	0.235	0.369	0.96	0.65
B	Upstream	0.716	0.225	1.03	0.65
	Effluent	0.241	0.579	0.93	1.55
	Downstream	0.727	0.404	1.65	0.65
C	Upstream	0.408	0.742	1.46	0.60
	Effluent	0.723	0.727	1.94	1.30
	Downstream	UDL	0.076	0.63	1.00
D	Upstream	1.380	0.041	1.77	0.45
	Effluent	26.900	0.250	49.60	110.75
	Downstream	UDL	0.371	0.91	0.75
E	Upstream	0.685	0.433	1.89	1.00
	Effluent	0.494	0.932	2.79	0.65
	Downstream	0.828	0.747	2.21	0.85
F	Upstream	0.272	0.235	0.56	0.85
	Effluent	8.360	3.530	12.80	28.25
	Downstream	UDL	0.170	0.51	0.85
G	Upstream	0.317	0.426	1.01	1.10
	Effluent	0.090	0.042	1.19	0.55
	Downstream	ND	ND	ND	ND
H	Upstream	UDL	0.195	1.00	0.55
	Effluent	1.220	0.047	3.26	1.45
	Downstream	UDL	0.498	0.92	0.80

I	Upstream	UDL	0.087	1.93	1.40
	Effluent	8.300	0.500	12.20	21.75
	Downstream	ND	ND	ND	ND
J	Upstream	UDL	0.117	0.76	0.95
	Effluent	1.710	0.290	4.89	2.50
	Downstream	0.950	0.960	4.26	4.90
K	Upstream	UDL	0.088	0.50	1.45
	Effluent	2.840	0.400	10.50	24.00
	Downstream	1.250	0.620	5.20	5.30

*ND = Not detected, UDL = under detection limit

The nitrogen and phosphorus content in the waters is a commonly used hydro chemical index for the assessment of the eutrophic potential of a river or lake (Chmiel et al., 2009). Normally, all the wet coffee processing plants we studied do not use any inorganic or organic chemicals during processing. As indicated in Table 2.4, at most of the sampling sites, the concentrations of NO_3-N, NH_4^+–N and TN increased from upstream of the coffee processing plant site to downstream of the effluent disposal site. The NO_3-N, NH_4^+-N, TN, and PO_4^{3-} concentration levels were found to vary from under the detection limit (0) to 26.9 mg/L; 0.041 to 3.53 mg/L; 0.50 to 49.6 mg/L; and 0.45 to 110.75 mg/L, respectively (Table 2.4). The decline in the NO_3-N concentration to zero mg/L (under the detection limit) at the downstream sites of the plants (C, D, F and H) may be due to denitrification by microbial action. The relatively higher nitrate concentrations (26.9 mg/L, 8.36 mg/L, 8.3 mg/L, and 2.84 mg/L in the effluents of the plants D, F, I and K, respectively) may occur as a result of the deamination of ammonium nitrogen from nitrogenous material that can be oxidized to nitrate by the action of microbiological agents (Morrison et al., 2001).

The PO_4^{3-} concentrations of the effluents vary within plants and are estimated to be huge for some plants as indicated in Table 2.4. For instance, PO_4^{3-} concentrations of 110.75 mg/L, 28.25 mg/L, 24.0 mg/L and 21.75 mg/L were measured for plants D, F, K and I, respectively, which is higher than for the other plants. This may be due to differences in pulping machines used by the plants, fermentation time and the amount of water used by these plants. The

concentrations observed in this study are much greater than in the findings of Endris et al. (2008) and Tekle et al. (2015), who reported a maximum PO_4^{3-} concentration of 9.9 mg/L and 18.5 mg/L, respectively. Thus, water bodies and ecosystems located downstream of the traditional wet coffee processing industries are at risk of eutrophication, which may have a huge impact on nearby residents and downstream aquatic organisms. Hence, urgent action should be taken, particularly in integrated coffee waste treatment and disposal as well as water resource management.

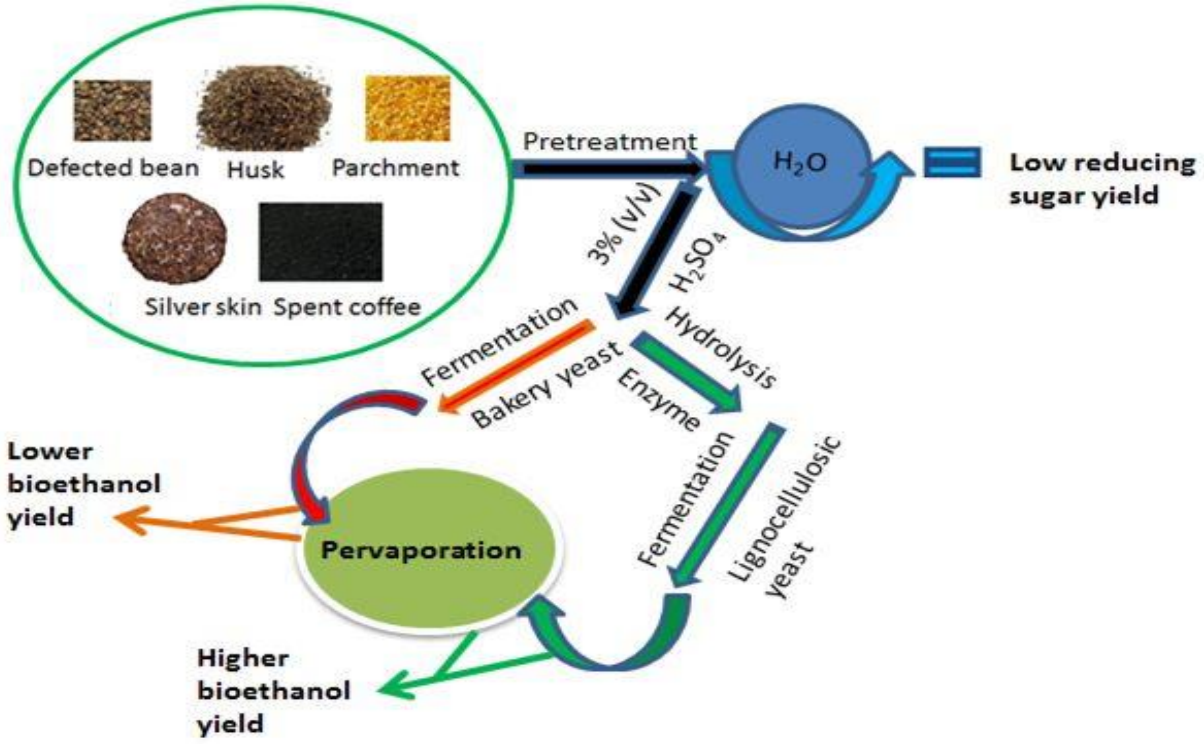
In general, a comparison of the NO_3-N, NH_4^+-N and TN, and PO_4^{3-} values found for upstream and downstream waters clearly shows that the NO_3-N, NH_4^+-N and TN, and PO_4^{3-} values increased in the downstream sites of certain plants. For example, NO_3^-N was found to increase in the downstream sites of plants B and E. NH_4^+-N was also measured to be higher in the downstream sites of plants A, B, D, E, H, J and K. Higher total nitrogen was measured at the downstream sites of plants A, B, E, J and K. Finally, higher PO_4^{3-} values were measured at the downstream sites of plants C, D, H, J and K than at the upstream sites. Thus, it can be concluded that wet coffee processing plant wastewater impacted the NO_3-N, NH_4^+-N and TN, and PO_4^{3-} concentration of downstream water bodies.

2.4 Conclusions

Overall, the coffee processing mills that were studied were found to be polluting water streams with high acidity, organic load (BOD_5 and COD), nutrients (nitrate and phosphate) and suspended solids. Comparisons between upstream and downstream sites demonstrated deterioration in river water quality, which may have an adverse effect on the aquatic life as a result of being a dumping site for untreated coffee processing wastewater. From the present study, it can be concluded that the wastewater released from wet coffee processing industries is not in agreement with either US-EPA or Ethiopian EPA guidelines, involving higher than recommended concentrations of most of the measured physicochemical parameters. As a result, the polluting potential of the factories is enormous at locations below effluent discharge points, even after stabilization in a disposal pit. Thus, in order to comply with the environmental regulations and achieve a restoration of the environment, it is necessary to find an economical and easily adaptable technology for the treatment of coffee processing wastewater. For example, by using the semi-washed processing, it is possible to reduce the water consumption and allows re-using of the wastewater. This, in turn, reduces the environmental burden and health problems of the local community. For this purpose, the government is expected to encourage wet coffee processing industry owners and local communities to follow and implement the semi-washed coffee processing method; since this method reduces the amount of water usage and no fermentation is needed, which in turn implies that it reduces the amount of water consumption needed for de-pulping, and wastewater (effluent) released from wet coffee processing industries. The government is also expected to critically follow whether the wet coffee processing industry owners are implementing the regulations (coffee quality control and transaction), and proclamations (to provide for coffee quality control and marketing) or not. Finally, the government (particularly, ministry of agriculture and Ethiopian EPA) should encourage them to construct waste water stabilization ponds (instead of disposal pits) to treat the wastewater created by these wet coffee processing industries by considering the amount of waste water released and carrying capacity of these ponds having different cells (anaerobic, facultative and maturation ponds).

3. Valorization of coffee byproducts for bioethanol production using lignocellulosic yeast fermentation and pervaporation

Graphical Abstract



Abstract

Industrial residue management is a critical element of sustainable development. In chapter 2, the impact of wet coffee processing industries wastewater on the downstream water bodies was addressed. The aim of this chapter is to investigate the potential of different coffee waste fractions for bioethanol fermentation and its purification by pervaporation; these fractions and the role of pervaporation in this application have not been studied before. Bioethanol production from different coffee waste fractions is studied here by acid or acid and enzymatic hydrolysis. The fermentation was conducted using two different yeasts (baker's yeast and lignocellulosic yeast). By using the cellulolytic enzymes and lignocellulosic yeast, a higher bioethanol yield was achieved. Further purification of the fermented filtrate was carried out by an alcohol selective pervaporation membrane at 4 temperatures (23, 30, 40 and 50 °C). Hydrolysis of the samples using cellulose complex and β-glucosidase enzymes and fermentation with lignocellulosic yeast, followed by purification using pervaporation resulted in a superior bioethanol yield of 51.7 ± 7.4 g/L for spent coffee and 132.2 ± 40 g/L for husk. Husk hydrolysis using cellulolytic enzymes and fermentation with lignocellulosic yeast, followed by product recovery through a pervaporation membrane, was found to be the optimal procedure, producing ethanol at a concentration of 132.2 ± 40 g/L. In general, husk hydrolysis using acid and cellulolytic hydrolysis and fermentation with lignocellulosic yeast GSE16-T18 followed by pervaporation was found to be the best process for producing the highest ethanol yield compared to the other fractions of coffee waste samples.

Keywords Coffee waste · Enzymatic hydrolysis · Pervaporation membrane · Pretreatment · Purification

3.1 Introduction

The global high energy demand has exerted an excessive stress on the use of non-renewable resources such as fossil fuels and various minerals (Loow et al., 2016b). The population growth (Gerland et al., 2014) and predictable depletion of the finite natural resources poses a great threat to long-term economic development and environmental safety. New renewable and environment-friendly sources of energy have been explored because of the depletion of fossil fuel reserves and concerns about climate change (Choudhary et al., 2016). The recent paradigm of sustainable development has resulted in intensive research on socially beneficial, economically viable and environmentally benign production technologies. As a result, agricultural waste has become a critical element of sustainable development, closely linking production and consumption. To support this goal, this chapter focuses on the possibilities of resource recovery by extraction of disposed coffee waste fractions for bioethanol production.

The global Energy demand is mainly fulfilled with conventional fossil fuels (66.2%), while biofuels from waste and other sources have only a minor contribution (12.7%) (International Energy Agency, 2012). However, burning fossil fuels releases CO_2 from historical stockpiles and accounts for about 70% of total climate harmful emissions (Balat et al, 2008).

Lignocellulosic biomass is plant-derived matter that is considered as a renewable carbon resource for the production of reducing sugar, which can be used as an alternative source for biofuels and chemicals (Loow et al., 2017). The development of second-generation biofuels from lignocellulosic biomass has many advantages from an energy and environmental point of view. The potential environmental benefits that can be obtained by replacing petroleum fuels with biofuels, derived from renewable sources of biomass, are the main driving forces for promoting the production and use of biofuels (Tiwari et al., 2015). Lignocellulosic biomass can be used for instance as a sustainable and cheap feedstock for the production of bioethanol, which will not only facilitate agricultural residue management but also provides fuel mainly for the transport sector (Rehman et al., 2014). Plant biomass is the most abundant renewable source of energy. However, it is largely wasted either by burning or by disposal in landfill sites, which results in huge production of greenhouse gases (Choudhary et al., 2016).

Biofuels appear to be one of the most viable and green alternatives among various renewable energy sources (Nigam and Singh, 2011). Production of biofuels, such as bioethanol, is a highly efficient pathway for reduction of crude oil demand and for environmental compliance (Achinas and Euverink, 2016). Bioethanol is a clean energy source that can be produced by fermentation of biomass (Verhoef et al., 2008). Bioethanol cannot only be used as fuel for energy generation, but also as a chemical in various industrial applications. Because of this broad potential, world bioethanol production has increased tremendously over the last decade (Chovau et al., 2013).

Agricultural waste contributes significantly to the global yield of lignocellulosic biomass (Loow et al., 2015). For example, the coffee industry generates huge amounts of coffee byproducts, which are rich in carbohydrates (cellulose, hemicellulose), proteins, pectins, bioactive compounds like polyphenols, and are cheap renewable resources (Murthy and Naidu, 2010). However, direct large-scale utilization of coffee waste around the world remains a challenge due to the presence of caffeine, free phenols and tannins (polyphenols) (Fan et al., 2003). Thus, alternative routes are needed for a feasible coffee waste management (Caetano et al., 2012).

There are challenges to resource recovery from lignocellulosic waste because the structure of lignocellulose is very resistant to degradation. This is due among others to cross-linking between the polysaccharides cellulose and hemicelluloses, and the lignin via ester and ether linkages (Lin and Tanaka, 2006). In order to overcome the recalcitrant structure of the biomass for effectively improving sugar recovery, a pretreatment stage is normally required (Loow et al., 2016b). When biomass is exposed to a pretreatment, several operations, such as the increase in the surface area and porosity, modification of the lignin structure, removal of lignin, partial depolymerization of hemicellulose, and reduction of cellulose crystallinity, can be accomplished (Loow et al., 2015).

Various pretreatment technologies have been extensively studied to process different types of biomass for cellulosic bioethanol production. None of those can be declared as optimal because each pretreatment has its intrinsic advantages and disadvantages. No standalone pretreatment option is available yet for commercial scale applications (Alvira et al., 2010). Acid pretreatment has been extensively and successfully investigated for several lignocellulosic

biomass fractions (Yaqoob et al., 2012). Diluted-acid hydrolysis is probably the most commonly employed and most effective method among the chemical pretreatment methods (Loow et al., 2016a). It can be used either as pretreatment to turn the lignocellulose more accessible for the cellulolytic enzymes or as the sole hydrolysis method to obtain fermentable sugars (Taherzadeh and Karimi, 2008). In addition, it is a favorable and cheap method for industrial application (Alvira et al. 2010). Therefore, for this study, dilute acid treatment was used for the production of bioethanol from coffee waste fractions.

Hexoses and pentoses are the main sources of monomeric sugars in the lignocellulosic hydrolysates. Monomeric hexoses are naturally fermented to bioethanol by *S. cerevisiae*, while the fermentation of pentoses is only done by other yeast species or by a few engineered *S. cerevisiae* strains harboring heterologous genes (Choudhary et al., 2016). Since the pentose sugars comprise a high percentage of the available sugars in lignocellulosic materials, its fermentation is essential for the economic conversion of lignocellulose to bioethanol (Jun and Jiayi, 2012).

The product stream after the fermentation step often denoted as the beer, consists of bioethanol, lignin, unconverted organic compounds, various inorganic soluble and water. Typical bioethanol concentrations reached after fermentation of lignocellulosic biomass is in the range of 3-6 wt. % (Balat et al., 2008). During purification, usually by distillation, the bioethanol is recovered from the beer to obtain fuel grade bioethanol. The energy requirement rapidly increases when the ethanol concentration in the beer falls below 5 wt. % (Madson and Lococo, 2000). Hence, alternative technologies can be considered. Among them, pervaporation is one of the most promising alternatives, due to the simplicity of operation, the absence of extra chemicals, low energy requirements and hence low operational cost (Bowen et al., 2007). Although distillation can achieve very high bioethanol recovery, it has some disadvantages when it comes to the purification of lignocellulosic bioethanol, i.e., a batch mode of operation and high energy requirement. Pervaporation can overcome these drawbacks and could therefore potentially replace the first distillation column (beer column) of the purification train (Chovau et al., 2013).

Therefore, in this chapter, valorization of coffee byproducts for bioethanol production using lignocellulosic yeast fermentation and pervaporation, is described in detail to answer the

research gap, which is indicated in section 1.6 of chapter 1. The study was conducted at the Department of Chemical Engineering of the University of Leuven (KU Leuven), Belgium from September 2014 to December 2015.

3.2 Materials and methods

3.2.1 Coffee waste collection

Coffee waste samples were collected in May and June 2014 from dry coffee processing plants in Jimma zone and Addis Ababa city, Ethiopia. This study included most coffee waste fractions (Figure 3.1). These are coffee husk (produced when coffee berries are processed by the dry processing method), coffee pulp (generated during wet coffee processing), parchment (produced when washed coffee is dried and deshelled), defected coffee beans (immature or overripe coffee bean which has poor quality), silver skin (produced when coffee bean is milled and roasted), and spent coffee ground (produced when roasted and grinded coffee bean is brewed).

Coffee husk and defected coffee beans were collected from Manna, Limmu Kossa and Gomma districts of Jimma zone in Ethiopia. The spent coffee samples were collected from Jimma town residential houses, staff lounge and student cafeterias of Jimma University, Ethiopia. The parchment and silver skin samples were collected from dry coffee processing plants in Addis Ababa, Ethiopia. All experimental procedures and experiments related to the dried coffee pulp (a byproduct of coffee waste fraction from wet coffee processing method) is fully considered in the next chapter (see chapter 4).

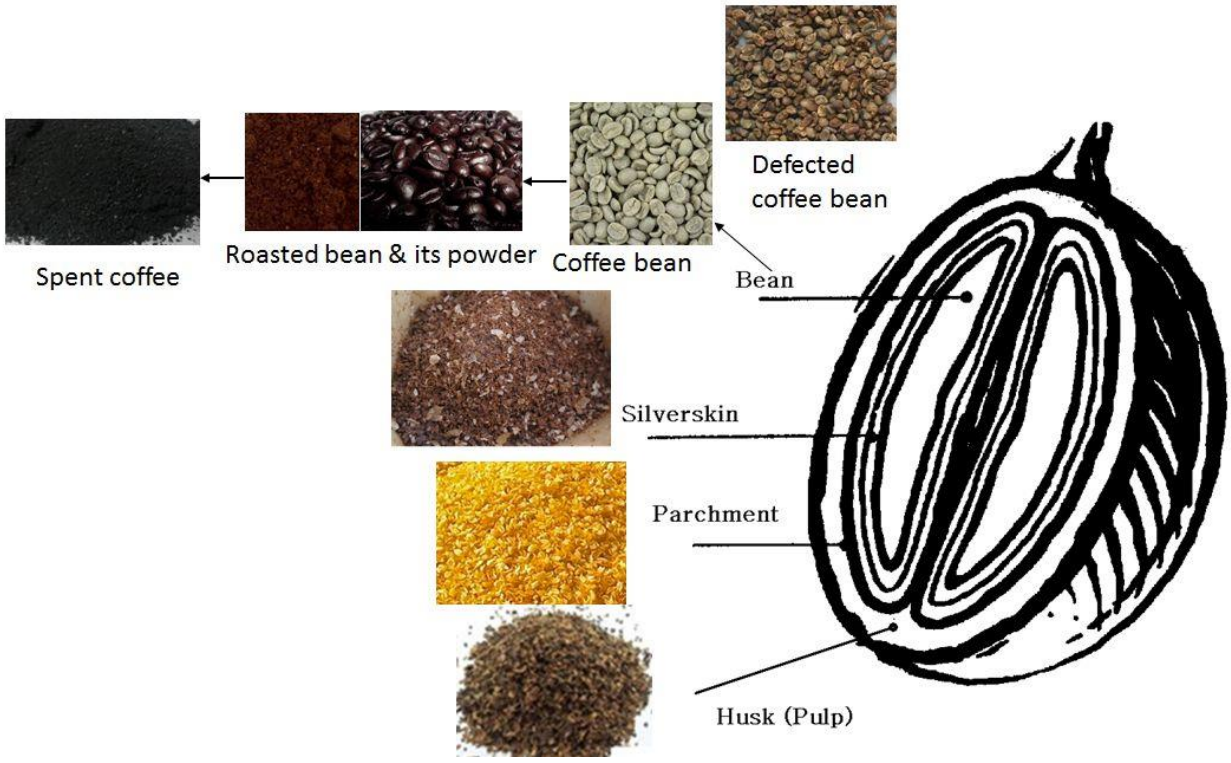


Fig. 3.1. Cross-section of coffee cherry and origin of the different coffee waste fractions.

Fresh samples of the coffee waste were collected from the chosen locations (coffee processing plants, cafeterias, and households). The samples were taken from five parts of the pile (i.e., from the bottom, top, left, right side and interior of the pile), and thoroughly ground and mixed to obtain homogeneous samples. Grinding was carried out with a coffee blender with grinder 'Seven 7 star' (Germany) to obtain particle sizes < 0.5 mm. The ground coffee waste samples were sieved with a U.S. standard sieve series mesh (ASTM E11-61, Tyler equivalent 32 inches mesh with 0.5 mm pore size, The W.S Tyler International Company, USA). All the coffee waste samples were air dried, ground and collected in well-dried polyethylene plastic containers and stored in a dry place until analysis.

3.2.2 Determination of physicochemical properties

The ground and sieved coffee waste samples were characterized by the following methods. The pH was determined using a Docu pH meter (Sartorius, Germany). For determination of electrical conductivity (EC), 5 g of air-dried ground coffee waste sample was transferred into a bottle and 25 ml of deionized water was added to obtain a suspension at 1:5 ratio. The bottles were capped and homogenized at 200 rpm for 15 min (D72379 Hechingen, Edmund Buhler GmbH®, Germany). The electrical conductivity (EC) was measured using pre-calibrated Hach HQ40d dual-input multi-parameter. For the determination of the moisture content, oven drying and a gravimetric method was used. Samples of fresh coffee waste were weighed and placed in a forced air oven at 105℃ for 24 h. After drying, the samples were weighed to determine the moisture content. The volatile suspended solids fraction (VSS) and ash content of the samples were determined by ashing the samples in a furnace (LH 60/13, Naberthem, Germany) at 550 °C for 1 hour. For the determination of biological oxygen demand (BOD) and chemical oxygen demand (COD), 1 g of grinded coffee sample was mixed with 10 ml of distilled water and they were determined using BOD HACH dilution method 8043 and dichromate reactor digestion method 8000, respectively.

3.2.3 Acid hydrolysis of coffee waste and fermentation using a baker's yeast

All five coffee waste samples (husk, silver skin, defected coffee bean, spent coffee, parchment) and their mixture were acid hydrolyzed with 3% (v/v) H_2SO_4 (99%, Sigma Aldrich) or distilled water and autoclaved (1 bar pressure, 121 ºC for 20 min) in a SystecV-150 autoclave (Systec, Germany). After the hydrolysis, samples were centrifuged and the supernatant was filtered using 0.2 µm filter. To verify the impact of the duration of autoclaving on the reducing sugar concentration, all samples hydrolyzed with 3% H_2SO_4 were autoclaved once and twice. The samples were then filtered and analyzed.

For determination of reducing sugar, the 3, 5-dinitrosalicylic acid (DNS) method (Miller, 1959) was used with a boiling water bath incubation (GP200, Grant, United Kingdom). The

absorbance (546 nm) was measured using a Genesys 10S UV-VIS spectrophotometer (Thermo Scientific, United States).

The acid pretreated materials from spent coffee and husk were neutralized with pure pellets of KOH (VWR International, United States) to pH 5 for fermentation. The baker's yeast (*Saccharomyces cerevisiae)* is commercial yeast distributed by Algist Bruggeman (Belgium) for bread making and other food applications. The final fermentation was conducted in an Erlenmeyer flask of 5 L with 2 L working volume. The filtered hydrolysate of the coffee waste was not supplemented with nutrients. The baker's yeast was pre-cultured overnight, and the cells were harvested by centrifugation for 10 min at 4000 rpm (Eppendorf 5810 R, Eppendorf AG, Germany). The dry weight of the harvested yeast was measured by drying a known amount of harvested wet yeast in an oven overnight (at about 105 °C) and the difference in mass was calculated. The dry weight of the baker's yeast used in this experiment was 2 g/L. For fermentation of the samples using baker's yeast, the samples were incubated at 30 °C and shaken at 250 rpm for 108 h (Incubator KB8182, Termaks, Norway).

For sugar and ethanol determination, samples were centrifuged at 14,000 rpm for 10 min and the supernatant was filtered using a 0.2 µm filter. The samples were stored at -20 °C prior to analysis. Ethanol and sugar concentrations were measured with an Agilent 1200 series HPLC with a refractive index detector, the column BioRad Aminex HPX-87H (7.8 9 300 mm) was kept at 40 °C. The eluent was 5 mM H_2SO_4 at a flow rate of 0.6 mL/min.

3.2.4 Enzymatic hydrolysis and fermentation using lignocellulosic yeast

The husk and spent coffee were first acid hydrolyzed using 3% (v/v) H_2SO_4 (99%, Sigma Aldrich) and autoclaved one time (1 bar pressure, 121 ºC for 20 min) in a SystecV-150 autoclave (Systec, Germany). The slurry was neutralized and the pH adjusted to 6 using pure pellets of KOH (VWR International, United States). The neutralized material was saccharified using 5% w/w (total solid) of cellulases from *Trichoderma reesei* ATCC26921 (NS50013, Novozymes, Denmark) and 0.5% w/w (total solid) of β-glucosidases from *Aspergillus niger* (C6105, Novozymes, Denmark). The saccharification was conducted at 50 °C and 160 rpm for 48 h.

The pH of the hydrolysate was adjusted to 5 using sulfuric acid (99%, Sigma Aldrich) and fermentations with the lignocellulosic yeast *Saccharomyces cerevisiae* GSE16-T18 (Demeke et al., 2013a; Demeke et al., 2013b) were carried out in Erlenmeyer flasks with different volumes (300 mL to 5 L) depending on the amount of hydrolysate to be fermented. The fermentation of samples with C5-degrading yeast GSE16-T18 (at a rate of 1 g dry yeast/liter of hydrolyzed solution) was carried out at 30 °C with shaking at 100 rpm. Incubation was done in an incubator shaker (Innova 4300, Brunswick Scientific, United States) at 30 °C with shaking and 100 rpm. Fermentation was performed for 96 h. Ethanol and sugar concentrations were measured with HPLC as previously mentioned.

3.2.5 Pervaporation

The acid treated and autoclaved samples were incubated and fermented in 5 L flasks. After fermentation of the samples using the two yeasts (baker's yeast and lignocellulosic yeast) independently, the filtrates were pervaporated using GFT GmbH pervaporating equipment. Permeate was collected every 30 min in a cold trap consisting of a U-glass immersed in liquid nitrogen inside a Dewar flask. At least three permeate samples under steady-state conditions were taken per experiment. The membranes were immersed in the feed solution at least 24 h prior to the experiment and then placed into the membrane test cell. For pervaporation of the filtered samples, an alcohol selective pervaporation membrane (Type POL_AL_M1, PolyAn GmbH, Germany), with a diameter of 58.78 mm, was used. The thickness of the membrane was measured by fowler ip54 caliper and was found to be 0.171 mm. The membrane used is dense. A dense membrane is usually a thin layer of dense material utilized in the separation processes of small molecules: usually in gas or liquid phase. Pervaporation of the fermented samples using baker's yeast (for spent coffee) and lignocellulosic yeast (for both spent coffee and husk) was conducted at 23, 30, 40 and 50 °C.

3.3 Results and discussion

3.3.1 Characterization of the coffee waste samples

The analysis of the different coffee waste samples is presented in Table 3.1. All coffee waste samples were observed to have a moisture content below 10% and a slightly acidic pH. Similar characteristics of coffee waste were also reported by the studies of Woldesenbet et al. (2014), which reported coffee pulp juice and mucilage having pH values of 4.75 and 3.67, respectively.

Table 3.1 Physicochemical characterization of coffee waste samples

Waste fraction	**No. Sample**	**MC (%)**	**pH**	**EC (µS/cm)**	**BOD (g/kg)**	**COD: BOD**	**VS (%)**	**Ash content (%)**
SS	3	1.05±0.265	5.4±0.12	917±135	8.61±0.19	4.3±1.03	89±1.1	11.5±1.1
Husk	4	4.70±0.229	4.6±0.10	1164±117	8.55±0.16	5.0±0.90	87±0.9	13.0±1.0
Parchment	8	6.33±0.162	5.6±0.07	365±82	8.42±0.12	2.5±0.63	92±0.7	7.7±0.7
DCB	3	3.23±0.265	5.7±0.12	875±135	9.34±0.19	10.7±1.03	87±1.1	13.2±1.1
SC	3	6.00±0.265	5.7±0.12	748±135	8.86±0.19	1.5±1.03	90±1.1	10.0±1.1
Mixture	3	5.33±0.265	5.1±0.12	923±135	9.08±0.19	2.0±1.03	89±1.1	11.0±1.1
F-test		69.8	19.4	7.7	4.6	11.6	6.5	6.5
P-value		<0.0001	<0.0001	0.0005	0.0073	<0.0001	0.0013	0.0013

MC = Moisture content; EC = Electrical conductivity; VS = Volatile solid; SS = Silver skin;
SC = Spent coffee; DCB= Defected coffee bean; Mixture = Mix of all of them in equal proportion

The COD:BOD ratio is frequently used as an indicator of biological degradability and the ratios below 5:1 indicate high digestibility (Woldesenbet et al., 2014). The COD:BOD ratios of most of the coffee waste samples were below 5:1, which indicates good biodegradability. The % volatile solid content of the waste fractions was in the range of 85 to 93 whereas the ash content ranged from 7 to 15%. These results are in agreement with a similar study (Woldesenbet et al.,

2014), which reported a volatile solid content of 90.2% and a fixed solid content of 9.8% for mucilage. The samples with the highest BOD and highest volatile solid content were selected and investigated for bio-ethanol production.

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3.3.2 Acid hydrolysis of the coffee waste samples

All samples (silver skin, spent coffee, husk, parchment and defected coffee beans) were mixed in a solid to liquid ratio of 1:10. Before autoclaving, the following observations were made. First, after the addition of distilled water, none of the samples dissolved and they floated on the water surface. However, after addition of 3% (v/v) H_2SO_4, DCB and husk formed a partial precipitation and the other samples (parchment, SS, and SC) did not precipitate at all and they remained on top of the water without getting settled in 3% (v/v) H_2SO_4. After autoclaving, all samples hydrolyzed with distilled water or 3% (v/v) H_2SO_4 gave a clear filtrate and clear precipitate. Thus, there is dissolution after autoclaving in both cases. Any sugar that acts as a reducing agent because of the presence of free aldehyde or ketone groups can be defined as a reducing sugar (Loow et al., 2016b). The reducing sugar yield determined by dinitrosalicylic acid (DNS) method of samples hydrolyzed with distilled water or diluted acid is presented in Figure 3.2.

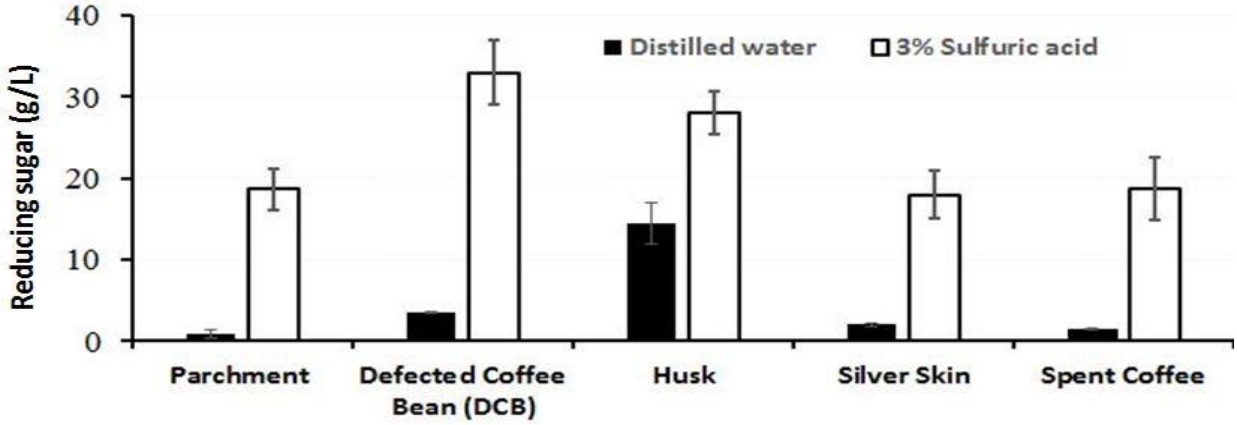


Fig. 3.2. Reducing sugar of coffee waste fractions pretreated with distilled water or 3% (v/v) H_2SO_4 at 121°C for 20 min

A higher amount of reducing sugar was released from the different coffee waste fractions with 3% (v/v) H_2SO_4 compared to distilled water (Fig. 3.2). Dilute acid hydrolysis effectively solubilizes hemicellulose and alters the biomass structure by interacting with the bonds between the biomass components (Limayem and Ricke, 2012). Dilute acid can also catalyze disruption of glucosidic bonds between sugar monomers within lignocellulosic biomass in the hydrolysis step (Aguilar et al., 2002). The mechanism of dilute acid hydrolysis in breaking down polysaccharides into monomers is based on the cleavage of the glycosidic linkages, defined as the ether bond which holds monomeric sugar units together in a polymer chain (Harmsen et al., 2010). Thus, dilute acid application can be extended in duration and strength to encompass both the pretreatment and hydrolysis step, resulting in total hydrolysis of lignocellulosic biomass into fermentable sugar monomers (Rehman et al., 2014). Hence, it is more advantageous to use dilute acid for the hydrolysis so that more reducing sugar can be obtained, which in turn increases the yield of bioethanol (Chovau et al., 2013). The reducing sugar yield was calculated using the method described by Miller (1959). The increase in total reducing sugar content that resulted from the acid hydrolysis is similar to the report of Navia et al. (2011). It is also reported that a higher reducing sugar yield (85.0%) is obtained with 3% (v/v) H_2SO_4 hydrolysis than with distilled water hydrolysis (56.7%) (Woldesenbet et al., 2014).

In addition, the results for the reducing sugar yield from the different coffee waste fractions (except for DCB and husk) are also in agreement with other similar experimental results of Urbaneja et al. (1996). They found a reducing sugar yield in the range of 0.65-21.81 g/L after acid hydrolysis of coffee pulp. However, our result is not in agreement with the other study findings of Ayele (2011), who reported that the amount of sugar obtained decreases as the acid concentration increases and reaches a maximum in acid-free (distilled water) hydrolysis. With 3% (v/v) H_2SO_4 hydrolysis, DCB and husk samples produced a higher yield in reducing sugar than spent coffee, parchment, and silver skin (Fig. 3.2). Since coffee husk and spent coffee are available in larger amounts than DCB, this study further continued with the former waste fractions.

3.3.3 Impact of autoclaving frequency on the yield of reducing sugars

The coffee waste samples were autoclaved once or twice to study the impact of the autoclaving frequency on fermentable sugar liberation and the amount of acetic acid produced. The results obtained from the HPLC analysis are presented in Table 3.2.

Table 3.2 Average results of the amount of sugars and acetic acid generated after single or double autoclaving of coffee samples

Coffee sample	Autoclaving Frequency	Glucose (g/L)	Xylose (g/L)	Arabinose (g/L)	Acetic acid (g/L)
Silver skin	Once	0.39	7.05	2.51	ND
	Twice	0.96	5.91	2.25	0.10
DCB	Once	1.53	5.20	1.71	ND
	Twice	1.57	4.99	1.77	ND
Parchment	Once	ND	9.41	ND	2.38
	Twice	0.25	12.65	ND	3.15
Spent coffee	Once	6.06	20.24	2.12	ND
	Twice	5.98	23.32	2.67	ND
Husk	Once	6.00	10.86	4.29	1.32
	Twice	5.47	8.74	4.19	1.19
Mixture	Once	1.67	12.41	2.61	ND
	Twice	1.66	12.35	2.60	ND

ND = Not Detected

Urbaneja et al. (1996) also reported about the concentrations of xylose (0.08-3.23 g/L), glucose (1.30-6.31 g/L), and arabinose (0.23-11.26 g/L) released by acid hydrolysis of coffee pulp. However, the amount of xylose found in this study is greater than the concentration indicated by Urbaneja et al. (1996). This may be due to differences in the type of coffee waste samples investigated. The amount of reducing sugars decreases when the samples were

autoclaved twice, while the amount of acetic acid increases (Table 3.2). In fact, for some of them, it is increasing.

The acetic acid production is probably due to the deacetylation of the hemicellulose by the intensification of the pretreatment. With the increasing of autoclaving, no significant gain in sugars was observed. Besides, it is a loss of energy and time. Thus, it is advisable not to increase the autoclaving frequency because it stimulates the formation of unwanted byproducts (Palmqvist & Hahn-Hägerdal, 2000), like acetic acid, which can affect the fermentation process. These compounds also limit efficient utilization of the hydrolysates for bioethanol production by microbial fermentation. In general, the acetic acid concentrations measured in our work (Table 3.2) are lower than those reported by the study of O'brien et al. (2004), who measured an acetic acid level of 6.2 g/L in corn fiber hydrolysate neutralized by lime.

3.3.4 Fermentation of spent coffee and husk produced by acid hydrolysis with baker's yeast

For this study, first, different conditions using baker's yeast to ferment husk and spent coffee samples were evaluated to select the optimum conditions. Both fractions were fermented for 108 h and samples were taken every 12 h. The optimal ethanol yield was obtained after 24 h of fermentation. The ethanol titers obtained were 4.30 g/L for husk and 7.08 g/L for spent coffee. Similar findings were also reported by (Ayele, 2011) with a maximum ethanol concentration of 7.4 g/L obtained in coffee pulp fermentation after 24 h. There was no production of acetic acid during the fermentation of spent coffee but there was the production of acetic acid at all stages of fermentation of husk resulting in a final value of 1.15 ± 0.54 g/L. Furthermore, the yield of ethanol from spent coffee is better than that from the husk. Thus, spent coffee was selected as the best candidate for the further fermentation (with baker's yeast) and pervaporation studies.

3.3.5 Impact of enzymatic hydrolysis on the yield of sugar

Cellulolytic enzymes were used to complement the acid hydrolysis (Table 3.2), aiming at a higher sugar level by digestion of both cellulose and hemicellulose. To determine the sugar

concentration after enzymatic hydrolysis, both spent coffee and husk samples were pretreated with sulfuric acid once and subsequently hydrolyzed with the enzymes. Glucose and xylose concentration was analyzed as a reference. Application of the enzymes resulted in higher sugar levels. Concentrations at time zero refer to the glucose and xylose concentration before enzymatic hydrolysis. The results are shown in Table 3.3.

Table 3.3 Glucose and xylose concentration after enzymatic hydrolysis of spent coffee and husk.

Time (h)	Husk		Spent coffee	
	Glucose (g/L)	Xylose (g/L)	Glucose (g/L)	Xylose (g/L)
0	6.0 ± 0.2	3.58 ± 0.03	6.0 ± 0.6	7.48 ± 0.06
12	6.0 ± 0.8	3.75 ± 0.03	7.0 ± 1.5	7.74 ± 0.15
24	10.0 ± 1.1	6.65 ± 0.30	15.5 ± 0.7	14.09 ± 0.73
36	11.3 ± 0.7	6.88 ± 0.06	15.8 ± 0.9	15.05 ± 0.39
48	11.5 ± 0.9	7.37 ± 0.05	16.0 ± 1.0	15.55 ± 0.09

Subsequently, both hydrolysates that were hydrolyzed for 48 h were fermented for 96 h and samples were taken every 12 h. The optimal ethanol yield was obtained after 12 h of fermentation; it was 47.9 g/L for spent coffee and 36.6 g/L for husk. Hence, by using the lignocellulosic yeast GSE16-T18, the bioethanol yield increased. In addition, acetic acid generation was not detected during the fermentation of spent coffee but there was the production of acetic acid at all stages of husk fermentation reaching a final value of 1.14 ± 0.28 g/L. The acetic acid is generated by a release of acetyl groups from the hemicellulose during the pretreatment of the biomass.

After the optimum ethanol concentration was obtained, the ethanol concentration was found to slightly decrease with time. This might be because the yeasts are shifting to use ethanol as a source of carbon. During husk fermentation, when the ethanol concentration reached an optimum, 3.56 ± 0.00 g/L xylose was remaining and no glucose was left, while for spent coffee, both glucose and xylose were fully consumed. To secure the fermentation medium from any source of possible contamination, only autoclaved and sterilized samples and equipment were used. Both the husk and spent coffee samples were selected for the pervaporation experiments.

3.3.6 Ethanol pervaporation of the fermented waste fraction

The total ethanol flux through the membrane increased with temperature (Table 3.4). Increasing the temperature typically produces an increase of the total and individual solute fluxes through the membrane due to the increase in vapor pressure and consequent increase in the driving force (Luis et al., 2013). Chovau et al. (2013) also reported that the total permeate flux significantly increases as the temperature increases.

Table 3.4 Permeate levels obtained after pervaporation of spent coffee fermentations (SCF) with baker's yeast

IC (feed solution) (g/L ethanol)	PT (°C)	PP (mbar)	CEAP (g/L)	TF (kg/h.m^2)
7 ± 0.08	23	4 ± 0.5	34.8 ± 1.3	1.05 ± 0.2
	30	3.6 ± 0.1	33.9 ± 0.4	0.88 ± 0.1
	40	4.6 ± 0.6	34.7 ± 2.1	1.28 ± 0.2
	50	5.6 ± 0.9	33.25 ± 0.1	1.56 ± 0.2

Note: IC = initial concentration; PT = pervaporation temperature; PP = pervaporation pressure at the permeate side; CEAP = concentration of ethanol after pervaporation; TF = Total Flux

The feed ethanol solution concentration was 7.00 ± 0.08 g/L (Table 3.4). In addition, the maximum level of ethanol obtained from the pervaporation of spent coffee using baker's yeast was 34.7 ± 2.1 g/L. Thus, the bioethanol level obtained is upgraded by a factor of 5 due to the pervaporation. The spent coffee samples were also hydrolyzed with the cellulolytic enzymes and fermented with the lignocellulosic yeast GSE16-T18. In this case, the ethanol level was 47.9 ± 0.06 g/L. Finally, the fermented broth was filtered and pervaporated at different temperatures (23, 30, 40 and 50 °C) and the results revealed that the total flux increases with temperature (Table 3.5).

Table 3.5 Permeate levels obtained after pervaporation of spent coffee samples hydrolyzed with cellulolytic enzymes (cellulase and β-glucosidase) and fermented with lignocellulosic yeast GSE16-T18

IC (feed solution) (g/L ethanol)	PT (°C)	PP (mbar)	Acetic acid (g/L)	CEAP (g/L)	TF (kg/h.m^2)
47.9 ± 0.06	23	12.6 ± 0.8	6.7 ± 0.4	51.7 ± 7.4	0.25 ± 0.03
	30	13.3 ± 0.4	7.2 ± 0.6	53.0 ± 4.6	0.37 ± 0.02
	40	14.3 ± 0.8	7.2 ± 0.1	47.5 ± 5.4	0.54 ± 0.02
	50	15.1 ± 0.7	6.7 ± 0.2	43.7 ± 1.6	1.24 ± 0.94

IC = initial concentration; PT = pervaporation temperature; PP = pervaporation pressure at the permeate side; CEAP = concentration of ethanol after pervaporation; TF = Total Flux

The feed ethanol solution concentration was 47.9 ± 0.06 g/L. The maximum concentration of ethanol obtained by pervaporation was 51.7 ± 7.4 g/L and this was obtained with pervaporation of the sample at room temperature. This shows that a much better ethanol yield from spent coffee samples was obtained when using cellulolytic enzymes (cellulase and β-glucosidase) and lignocellulosic yeast compared to using only baker's yeast.

The total flux also increased with temperature, however, the increment of temperature did not increase the bioethanol yield (Table 3.6). The feed ethanol solution concentration and the maximum ethanol produced were found to be 36.6 ± 0. 2 g/L, and 132.2 ± 40 g/L, respectively, after pervaporation of the sample at room temperature. Hence, it was observed that bioethanol production is upgraded by a factor of 3.5 when using pervaporation. Similarly, O'Brien et al. (2004) reported the production of 150-170 g/L ethanol from corn fiber hydrolysate fermentations followed by pervaporation.

Table 3.6 Permeate levels obtained after pervaporation of husk samples hydrolyzed with cellulolytic enzymes (cellulase and β-glucosidase) and fermented with lignocellulosic yeast GSE16-T18

IC (feed solution) (g/L ethanol)	PT (°C)	PP (mbar)	Acetic acid (g/L)	CEAP (g/L)	TF (kg/h.m^2)
36.6 ± 0.02	23	12.8 ± 0.27	14.3 ± 2	132.2 ± 40	0.66 ± 0.30
	30	16.7 ± 2.92	10.5 ± 2	50.5 ± 24	0.56 ± 0.05
	40	18.9 ± 0.85	8.5 ± 0.2	36.4 ± 0.8	0.85 ± 0.07
	50	18.5 ± 0.84	9.1 ± 0.5	37.7 ± 0.1	1.32 ± 0.03

IC = initial concentration; PT = pervaporation temperature; PP = pervaporation pressure at the permeate side; CEAP = concentration of ethanol after pervaporation; TF = Total Flux

As indicated in Table 3.7, production of ethanol by fermentation and pervaporation of both spent coffee and husk was quite satisfactory in comparison with literature data for other substrates. The ethanol yield obtained after husk hydrolysis with cellulolytic enzymes (cellulase and β-glucosidase), fermentation with lignocellulosic yeast GSE16-T18, and pervaporation resulted in a yield of 132.2 ± 40 g/L, which is similar to the ethanol obtained from corn fiber (150-170 g/L) with the same processes (O'Brien et al., 2004). Ethanol produced after pervaporation was found to be significantly lower when the pervaporation temperature was increased. This is due to the difference in pressure at the permeate side. Since the pressure at the permeate side is very variable between experiments, the driving force for pervaporation of the ethanol also varies quite strongly, which can explain the different concentrations of ethanol in the permeate.

Fermentation media are often complex and may result in membrane fouling. Fouling is defined as a reduction in the rate of permeation with the time of membrane operation (Qureshi and Blaschek, 1999a). Pervaporation membranes are often sensitive to the fermentation broth components, which are very complicated, and consist of microorganisms and fermentation nutrients, by-products, and inhibitors (Vane, 2005; Yi et al., 2015). These complicated

components can affect the separation performance of bioethanol from broths (Yi and Wan, 2017). Numerous researchers reported either a positive or negative impact of fermentation by-products and inhibitors on the pervaporation performance using different membrane materials (Aguilar-Valencia et al., 2012; Gaykawad et al., 2013; Chen et al., 2014; Fan et al., 2014; Yi et al., 2015).

Several studies have also reported pervaporation membrane fouling in a fermentation-pervaporation coupled processes (Qureshi and Blaschek, 1999a; Qureshi and Blaschek, 1999b; Huang and Meagher, 2001; Qureshi et al., 2001). Accordingly, Liu et al. (2011) reported that membrane fouling was related to adsorption of active cells on the membrane surface, and it could be accelerated by microbial growth and metabolism in the live fermentation broth. However, membrane fouling could be easily removed by a simple water rinse, which properly restored the pervaporation performance of the membrane. Besides, the studies of O'Brien and Craig Jr (1996) also confirmed that periodic cleaning of the membranes improved the consistency of performance of the pervaporation operation and minimized problems due to fouling.

The results from this investigation also demonstrate that coffee husk and spent coffee can be used as an alternative substrate for ethanol production, in comparison to different biomass resources (Barley straw, 10 g/L; Wheat stillage, 11 g/L; sweet sorghum bagasse, 16.2 g/L; corn stover, 16.8 g/L; wheat straw, 18.1; Korean food waste leachate, 24.17 g/L, kitchen waste, 30 g/L and coffee pulp, 7.4 g/L) (Table 3.7).

Table 3.7 Comparison of ethanol yields obtained after enzymatic hydrolysis, fermentation and pervaporation of various substrates, as reported in the literature with the results obtained in the present study

Residue	**Ethanol concentration (g/L)**	**Reference**
Corn stalks	5	(Belkacemi et al., 2002)
Anaerobic digested sludge	10	(Bashiri et al., 2016)
Barley straw	10	(Belkacemi et al., 2002)
Wheat stillage	11	(Davis et al., 2005)
Sweet sorghum bagasse	16.2	(Ballesteros et al., 2004)
Corn Stover	16.8	(Öhgren et al., 2007)
Wheat straw	18.1	(Ballesteros et al., 2004)
Korean food waste leachate	24.17	(Le Man et al., 2010)
Kitchen waste	30	(Tang et al., 2008)
Coffee pulp	7.4	(Ayele, 2011)
Corn fiber hydrolysate fermentations by pervaporation	150 -170	(O'brien et al., 2004)
Spent coffee fermentation with bakery yeast	7 ± 0.08	This study
Spent coffee fermentation with bakery yeast and pervaporation	34.7 ± 2.1	This study
Spent coffee hydrolysis with cellulolytic enzymes and fermentation with lignocellulosic yeast GSE16-T18	47.9 ± 0.06	This study

Spent coffee hydrolysis with cellulolytic enzymes and fermentation with lignocellulosic yeast GSE16-T18 and then pervaporation	51.7 ± 7.4	This study
Husk fermentation with bakery yeast	4.3 ± 0.03 g/L	This study
Husk hydrolysis with cellulolytic enzymes and fermentation with lignocellulosic yeast GSE16-T18	36.6 ± 0. 02	This study
Husk hydrolysis with cellulolytic enzymes and fermentation with lignocellulosic yeast GSE16-T18 and then pervaporation	132.2 ± 40	This study

3.4 Conclusions

This chapter describes the bioethanol yield from different coffee waste fractions obtained by fermentation with *Saccharomyces cerevisiae* baker's and lignocellulosic yeasts, followed by product purification by an alcohol selective pervaporation membrane. No earlier work has reported bioethanol production from coffee waste fractions by pervaporation for purification of the fermented broth. The results of the study revealed that pervaporation resulted in a bioethanol yield of 132.2 ± 40 g/L from coffee husk at the optimum conditions. This is promising for future studies in bioethanol production and pervaporation technology. The utilization of coffee waste fractions for bioethanol production is a sustainable and eco-friendly approach for renewable biofuel production. The results from this investigation also demonstrate that coffee husk and spent coffee can be used as an alternative substrate for ethanol production, in comparison to different biomass resources. This result is very promising and could be improved further by using distillation and hydrophilic membranes for pervaporation. Further research is also needed to examine the economic viability of the process.

4. Production of bioethanol by pervaporation of the fermentation broth of dried coffee pulp

Abstract

In the previous chapter, the potential of coffee byproducts (husk, parchment, silver skin, defected coffee bean and spent coffee ground) for bioethanol production and quality upgrading by pervaporation membrane was evaluated. This chapter evaluates the potential of dried coffee pulp for bioethanol production and upgrading the quality of the produced ethanol by using a pervaporation membrane. Coffee pulp was ground and pretreated with different concentrations of diluted H_2SO_4 (0, 1, 2, 3, 4, 5 and 10 vol %) at different solid: liquid ratios (1:1, 1:2, and 1:4). The neutralized hydrolysate was fermented using *S. cerevisiae* and lignocellulosic yeast GSE16-T18 strain. Before fermentation of the hydrolysate with the lignocellulosic yeast, the enzyme accellerase was used for hydrolysis. The fermented feed solution was filtered and pervaporated at different temperatures (30, 40, 50 and 60 °C) using the PolyAn POL_AL_M1 pervaporation membrane. Neutralization of the autoclaved hydrolysates, which were mixed in a 1:2 solid to liquid ratio to a pH value of 5 enhances the glucose concentration by 5.5%, 5.4% and 8.3% only for solutions mixed with 1%, 2% and 3% H_2SO_4, respectively. The optimum ethanol yield (7.03 ± 2.63 g/L) was obtained after 12 h of fermentation with lignocellulosic yeast GSE16-T18 strain. Furthermore, pervaporation of the fermented feed concentrated the ethanol to 15.47 ± 0.66 g/l indicating that dried coffee pulp can be a suitable candidate for the production of bioethanol. In general, the membrane flux and water/ethanol separation factor were found to increase with increasing pervaporation temperature. The result of the finding indicates that pervaporation needs to be further improved by enhancing the ethanol selectivity. Hence, the pervaporation potential is estimated by simulation.

Keywords: Coffee pulp; lignocellulosic bioethanol; lignocellulosic yeast; enzyme hydrolysis; fermentation; pervaporation

4.1 Introduction

As the economy of the world is highly dependent on fossil energy sources (Uihlein and Schebek, 2009) and its excessive consumption has resulted in generation of high levels of pollution (Ballesteros et al., 2006) the need to seek new alternatives to cover the future energy demand is considerably high (Navia et al., 2011). An alternative fuel must be technically feasible, economically competitive, environmentally acceptable, and readily available (Demirbas, 2008). In this regard, Uihlein and Schebek (2009) indicated that biomass is a sustainable alternative to fossil energy carriers, with the potential to produce fuels, electricity, chemicals, and other goods. The development of fuel production processes from renewable resources is one of the most promising ways to replace fossil fuels and reduce greenhouse emissions (Amelio et al., 2016).

Coffea arabica L. has its origin and diversity in the Afromontane rainforests of southwestern Ethiopia (Yadessa, 2014). Coffee is the world's most important legally traded agricultural commodity (Vega, 2008). About 80 tropical countries produce and export coffee, generating a significant income (Tesfaye et al., 2014). It plays a significant role in the Ethiopian economy, contributing over 35 % of the total export value; 4 to 5% to the national Gross Domestic Product and generating 20% of government revenue (Petit, 2007). It is a source of income for over one million coffee growing households, and over 15 million people derive their livelihood directly or indirectly from this crop along the value chain (Petit, 2007).

The coffee industry is responsible for generating large quantities of residues, among which coffee pulp, coffee husk, spent coffee grounds and coffee silver skin are the most significant (Ballesteros et al., 2014). In this regard, the studies of Murthy and Naidu (2010) also indicated that the coffee industry liberates enormous amounts of coffee byproducts, which are rich in carbohydrates, proteins, pectins, bioactive compounds like polyphenols and may have potential as cheap, renewable resources. However, large-scale utilization and management of coffee waste around the world still remain a challenge due to its content of caffeine, free phenols and tannins (polyphenols) (Fan et al., 2003).

Previous studies reported that wet coffee processing industries have a severe impact on the environment, generating different types of residues: pulp, mucilage, hulls and residual water

(Rojas et al., 2002; Haddis and Devi, 2008; Beyene et al., 2012). Coffee pulp is the first by-product obtained during processing and represents 29% dry-weight of the whole berry. It is obtained during wet processing of coffee and for every two tons of coffee produced, one ton of coffee pulp is obtained (Roussos et al., 1995). The organic components present in coffee pulp (dry weight) include tannins 1.80–8.56%, total pectic substances 6.5%, reducing sugars 12.4%, non-reducing sugars 2.0%, caffeine 1.3%, chlorogenic acid 2.6%, and total caffeic acid 1.6% (Murthy and Naidu, 2012).

The crucial step in the production of biofuels from lignocellulosic biomass is pretreatment. The choice of the optimum pretreatment process depends on the feedstock and its economic assessment and environmental impact. For this purpose, a detailed review conducted by Menon and Rao (2012) indicated that even though there are different pretreatment categories (including biological, mechanical, chemical methods and various combinations thereof) for the biofuel industry, none of those is outstanding as each pretreatment has its intrinsic advantages and disadvantages. In this regard, it has been demonstrated that dilute acid prehydrolysis can achieve high reaction rates in a short time and significantly improve cellulose hydrolysis (Xiang et al., 2003). Dilute sulfuric acid pretreatment (Teramoto et al., 2009) was used to disorganize the crystalline structure and recalcitrant nature of coffee pulp in order to release the polymer chains of cellulose and hemicelluloses for facilitating enzymatic attack. Menon and Rao (2012) also pointed out that the most commonly used acid, dilute sulphuric acid (H_2SO_4), has been commercially used for the pretreatment of a wide variety of lignocellulosic materials. When pervaporation is an appropriate technique to perform the separation of multicomponent mixtures, the study of Luis and Van der Bruggen (2015) emphasizes the importance of a closer evaluation of the thermodynamic properties of the mixture and the effect that the membrane is producing in the separation.

Therefore in this chapter, to answer the research gap, which is indicated in section 1.6 of chapter 1, the production of bioethanol from the fermentation broth of dried coffee pulp and then quality upgrading by using an alcohol selective pervaporation membrane is described in detail.

4.2 Materials and methods

4.2.1 Coffee waste collection

Dried coffee pulp sample was collected from wet coffee processing industries located in the Kersa district of Jimma zone, Ethiopia. Coffee pulp is the byproduct obtained when the washed coffee bean is deshelled using the wet processing method. Fresh samples of coffee pulp were collected and thoroughly mixed to obtain homogeneous samples. The samples were then air dried and grinding was carried out with a coffee blender with grinder 'Seven 7 star' (Germany). To obtain a particle size < 0.5 mm, the ground coffee waste samples were sieved with a U.S. standard sieve series mesh (ASTM E11-61, Tyler equivalent 32 inches mesh with 0.5 mm pore size, The W.S Tyler International Company, USA). The ground samples were collected in well-dried polyethylene plastic containers and stored in a dry place until analysis.

4.2.2 Determination of physicochemical properties

The ground and sieved coffee waste samples were characterized by the following methods. The pH was determined using a Docu pH meter (Sartorius, Germany). For determination of the electrical conductivity (EC), 5 g of air-dried ground coffee pulp was transferred into a bottle and 25 ml of deionized water was added to obtain a suspension at 1:5 ratio. The bottles were capped and homogenized at 200 rpm for 15 min (D72379 Hechingen, Edmund Buhler GmbH®, Germany). The electrical conductivity (EC) was measured using a pre-calibrated Hach HQ40d dual-input multi-meter. For the determination of the moisture content, oven drying and a gravimetric method were used. Samples of fresh coffee waste were weighed and placed in a forced air oven at 105 °C for 24 h. After drying, the samples were weighed to determine the moisture content. The volatile suspended solids fraction (VSS) and ash content of the samples were determined by ashing the samples in a furnace (LH 60/13, Naberthem, Germany) at 550 °C for 1 hour.

4.2.3 Hydrolysis of coffee waste

Acid hydrolysis is an often proposed pretreatment method for the decomposition of lignocellulose (van der Pol et al., 2014). The dried coffee pulp samples were pre-treated with distilled water, 1%, 2%, 3%, 4%, 5% and 10 % (v/v) H_2SO_4 (99%, Sigma Aldrich) by varying the solid to liquid ratio (1:1, 1:2, and 1:4). The samples were then autoclaved (1 bar overpressure, 121 ºC for 20 min) in a SystecV-150 autoclave (Systec, Germany). Pretreatment is required to increase the surface area of the feedstock, thereby rendering the lignocellulose accessible for hydrolysis (Klinke et al., 2004). After pretreatment, samples were centrifuged and the supernatant was filtered using a 0.2 µm filter. Acid pre-treated coffee pulp was neutralized with KOH (VWR International, United States) to a pH of 5 before fermentation with *S. cerevisiae*. For fermentation with lignocellulosic yeast, the coffee pulp sample was neutralized at a pH of 5.1, and then saccharified using the enzyme accellerase® TRIO™ (0.1 ml of the enzyme per gram of biomass). The saccharification was conducted at 50 °C and 160 rpm for 48 h. For determination of reducing sugar, an Agilent 1200 series HPLC was used.

4.2.4 Fermentation

Fermentations with baker's yeast (Bruggeman, Belgium) and with lignocellulosic yeast GSE16-T18 (Demeke et al., 2013a; Demeke et al., 2013b) were carried out in Erlenmeyer flasks with different volumes (100 mL to 5 L) depending on the amount of hydrolysate to be fermented. The final fermentation was conducted in an Erlenmeyer flask of 5 L with 1.75 L of working volume. The filtered hydrolysate of the coffee waste was not supplemented with nutrients. The baker's yeast was pre-cultured overnight, and the cells were harvested by centrifugation for 10 min at 4000 rpm (Eppendorf 5810 R, Eppendorf AG, Germany). The dry weight of the harvested yeast was measured by drying a known amount of harvested wet yeast in an oven overnight (at about 105 °C) and the difference in mass was calculated. The dry weight of the baker's yeast used in the experiment was 4 g/L. For fermentation of the samples using baker's yeast, the samples were incubated at 30 °C and shaken at 250 rpm for 24 h (incubator KB8182, Termaks, Norway).

Before fermentation of the samples using lignocellulosic yeast GSE16-T18, the samples were first further hydrolyzed using the enzyme accellerase® TRIO™ (DuPont). The optimum hydrolysis time was found to be 48 h. Incubation was done in an incubator shaker (Innova 4300, Brunswick Scientific, United States). The fermentation of samples with C5-degrading yeast GSE16-T18 (at a rate of 1 g dry yeast/liter of hydrolyzed solution) was carried out at 30 °C with shaking at 100 rpm and stopped after 12 h, since this time was found to be optimal for ethanol production.

For sugar and ethanol determination, samples were centrifuged at 14,000 rpm for 10 min and the supernatant was filtered using a 0.2 µm filter. The samples were stored at -20 °C prior to analysis. Ethanol and sugar concentrations were measured with an Agilent 1200 series HPLC with a refractive index detector, the column BioRad Aminex HPX-87H (7.8 × 300 mm) was kept at 40 ºC. The eluent was 5 mM H_2SO_4 at a flow rate of 0.6 mL/min.

4.2.5 Pervaporation

After fermentation of the samples, the fermented broth was centrifuged, and then filtered using a coffee filter to remove the remaining suspended solids, and then pervaporated using two pervaporation instruments: Sulzer Chemtech AG (PERVAP^{TM} LZ 2013 PV Pol.22, Switzerland), and GFT GmbH, Germany operating at different pervaporation pressures. The operating pressure above the active layer of the membrane is atmospheric pressure or slightly higher caused by the pressure drop in the membrane cell but no overpressure was applied. In the other side of the membrane (permeate), a vacuum pressure lower than 20 mbar was achieved by means of a 2-stage vacuum pump. Permeate was collected every 30 min in a cold trap. At least duplicate permeate samples under steady-state conditions were taken per experiment. The membranes were immersed in the feed solution at least 24 h prior to the experiment and then placed into the membrane test cell (Chovau et al., 2011; Luis et al., 2013).

For pervaporation of the filtered samples, an alcohol selective pervaporation membrane (Vane, 2005) Polyvinyl alcohol type M1 (POL_AL_ M1, PolyAn GmbH, Germany), with a total and active diameter of 75.6 and 70 mm, respectively, was used. The total thickness of the

membrane was measured by fowler ip54 caliper and was found to be 0.171 mm. Pervaporation of the fermented samples was conducted at 30, 40, 50 and 60 °C. The membrane flux J (kg h^{-1} m^{-2}) was determined gravimetrically using a balance with an accuracy of 10^{-4} g by weighing the mass of permeate w (kg) obtained during the collecting time Δt (h):

$J = \frac{w}{\Delta t * A}$; where A is the effective surface area (Steinigeweg and Gmehling, 2004).

The separation factor was calculated as the ratio of the molar component concentrations in the permeate (y_i) and feed (x_i) solutions:

$\beta \frac{i}{j} = \frac{y_i / y_j}{x_i / x_j}$ (Jiménez et al., 2002)

The experimental flux for each component was calculated as:

$Ji = J * y_i * \frac{m_i}{m_t}$, with m_i and m_t being the molecular weight of the component i and the mixture, respectively (Švandová and Markoš, 2011).

The partial molar flux for each component ji (cm^3(STP)$cm^{-2}s^{-1}$) was calculated from (ignoring simple conversion terms, m^2 to cm^{-2}, l to cm^3, h to s):

$j_i = \frac{J_i * v_i^G}{m_i}$; where v_i^G is the molar volume of gas i (22.4 l (STP) mol^{-1} and m_i is the molecular weight of component i (Jiménez and Costa-López, 2002).

The permeance was calculated according to the following equation:

$\frac{P_i}{l} = \frac{j_i}{\left(x_i * \gamma_i * p_i^o - y_i * P_p\right)}$; Where, P_i is the permeability coefficient, l is the membrane thickness, P_i^o is the vapor pressure and p_p is the pressure in the permeate side measured experimentally during the experiment and the activity coefficient γi for each component have

been calculated using UNIQUAC as the thermodynamic model (Steinigeweg and Gmehling, 2003).

The selectivity of the membrane was calculated from the ratio between permeances:

$\alpha \frac{i}{j} = \frac{P_i / l}{P_j / l} = \frac{P_i}{P_j}$ (Bessling et al., 1998).

4.2.6 Simulation

The alternative of using a hydrophobic membrane to purify the downstream of the fermentation reactor is in using a series of distillation columns followed by hydrophilic membranes. Energy requirements of possible industrial cases were calculated in an environmental simulator. The pervaporation unit was simulated with the component splitter of Aspen Plus version 7.3 (Luis et al., 2014), while the distillation columns were simulated using the Radfrac model of Aspen Plus version 7.3 and the UNIQUAC model was used as a thermodynamic model.

4.3. Results and discussion

4.3.1 Characterization of the coffee waste samples

The air-dried and ground coffee pulp sample used for analysis has the following characteristics: electrical conductivity (EC), pH, biological oxygen demand (BOD), and chemical oxygen demand (COD) results were measured to be 1790 ± 10 µS/cm, 8.76 ± 0.23, 4200 ± 12 g/kg, and 5880 ± 14 g/kg, respectively. Furthermore, the moisture content was 8.05 ± 0.10; the ash content was 20.14 ± 0.14%, and the volatile solid content was 79.86 ± 0.14%. For comparison, the study conducted by Woldesenbet et al. (2014) on coffee pulp juice and mucilage reported a volatile solid content of 66.5 and 90.2 %, respectively. In general, dried coffee pulp has a higher pH, higher EC, higher BOD, lower volatile solid content, and a higher ash content than all the other coffee waste fractions as indicated in chapter 3 section 3.3.1.

4.3.2 Hydrolysis of the coffee waste samples

The samples were pretreated with either distilled water or using different concentrations of H_2SO_4 (v/v) (1 %, 2 %, 3 %, 4 %, 5 %, and 10 %), and finally autoclaved. Among the samples mixed in a solid to liquid ratio of 1:1, 1:2, and 1:4, the samples mixed in a 1:1 ratio yielded no filtrate at all and they were excluded from further study. The results of hydrolysis of the remaining samples are indicated in Table 4.1. These results indicate that the hydrolysate is composed of more xylose and arabinose than glucose.

Table 4.1. Mean results of hydrolysis of samples pretreated with distilled water alone, different concentrations of % H_2SO_4 (v/v) and autoclaved

% H_2SO_4 used	Sample ID	Solid: Liquid ratio	Glucose (g/L)	Xylose (g/L)	Arabinose (g/L)	Xylitol (g/L)	Glycerol (g/L)	Acetic acid (g/L)
0 (DW)	A1	1:4	0.35 (0.00)	1.32 (0.23)	0.00	0.00	0.16 (0.01)	0.74 (0.05)
1	B1	1:4	0.39 (0.10)	0.25 (0.00)	2.97 (0.31)	0.00	0.18 (0.00)	0.47 (0.13)
2	C1	1:4	1.04 (0.20)	4.86 (1.03)	5.92 (1.40)	0.09 (0.01)	0.25 (0.01)	1.28 (0.03)
3	D1	1:4	2.25 (0.60)	11.27 (1.50)	6.26 (1.42)	0.19 (0.00)	0.26 (0.00)	2.09 (0.40)
4	E1	1:4	2.76 (0.70)	13.73 (1.46)	6.51 (1.65)	0.29 (0.05)	0.26 (0.10)	2.52 (0.90)
5	F1	1:4	3.15 (1.05)	14.14 (2.60)	6.27 (1.39)	0.37 (0.08)	0.28 (0.03)	2.77 (0.40)
10	G1	1:4	4.15 (0.69)	14.37 (1.82)	5.35 (1.97)	0.67 (0.04)	0.40 (0.07)	3.69 (0.55)
0 (DW)	A2 *	1:2	-	-	-	-	-	-
1	B2	1:2	0.73 (0.01)	1.71 (0.21)	0.82 (0.00)	0.00	0.26 (0.01)	0.26 (0.01)
2	C2	1:2	1.12 (0.10)	4.25 (0.23)	10.07 (1.01)	0.00	0.50 (0.11)	0.35 (0.20)
3	D2	1:2	2.05 (0.32)	11.53 (2.10)	10.52 (1.30)	0.32 (0.10)	0.41 (0.05)	2.42 (0.40)
4	E2	1:2	4.15 (1.01)	20.18 (2.32)	11.09 (1.32)	0.49 (0.02)	0.43 (0.04)	3.70 (0.62)
5	F2	1:2	4.50 (0.71)	22.93 (3.01)	10.93 (2.31)	0.52 (0.01)	0.41 (0.00)	4.19 (0.33)
10	G2	1:2	6.33 (0.54)	24.99 (2.71)	9.61 (2.24)	0.59 (0.22)	0.55 (0.20)	5.27 (0.84)

DW = Distilled water; * = no filtrate was obtained

* Values outside of the bracket are the mean results and those in brackets are the standard deviation values

As shown in Table 4.1, the amount of glucose, xylose and arabinose that can be obtained by hydrolysis of the sample using distilled water alone is lower than using H_2SO_4. Furthermore, Table 6.1 indicates that as the amount of H_2SO_4 is increasing (from 1%, 2%, 3%, 4%, 5%, and 10%), the amount of glucose, xylose, arabinose, xylitol, glycerol, and acetic acid is enhanced for both the 1:4 and 1:2 solid to liquid ratio. Thus, it can be observed that as the yield of fermentable sugars (glucose, xylose, and arabinose) increases, the concentration of byproducts (xylitol, glycerol and acetic acid) is also enhanced. In comparison, Klinke et al. (2004) confirmed that decomposition of lignocellulose to acquire monomeric sugars results in the formation of a large amount of byproducts.

The study by Urbaneja et al. (1996) on coffee pulp hydrolysates reported concentrations of xylose in the range between 0.08 and 3.23 g/L, arabinose between 0.23 and 11.26 g/L, glucose between 1.30 and 6.31 g/L, and fructose between 0.90 and 3.00 g/L. Furthermore, the study by Gurram et al. (2016) on coffee pulp from Mexico reported sugar contents, expressed as percentages of dry mass, of 5.8, 5.2, 20.2, 4.2, and 4.7 % for arabinose, galactose, glucose, xylose, and mannose, respectively. From these yields, it can be observed that the coffee pulp hydrolysates obtained in this study are different from the studies mentioned above. An explanation for this difference was given by Navia et al. (2011) who reported that the chemical composition of coffee byproducts changes according to the plantation's height above mean sea level, and at the same time, the composition also changes according to the type of coffee and the stage of development of the fruit (mature/immature, defected, ripe/unripe) when it is harvested. Thus, the coffee beans considered in this study are different from the others since it is a dried and ground Arabica coffee bean collected from wet coffee processing industries in Jimma, Ethiopia, at a latitude and longitude of 7°40′N 36°50′E, and it has a tropical rainforest climate.

4.3.3 Impact of neutralization of the autoclaved samples and formation of degradation products

The pH of wet coffee pulp was measured to be 5.69 ± 0.18 (slightly acidic). However, after it is air dried and grinded, the pH was 8.76 ± 0.23 (slightly alkaline). The cause of this pH variation might be the volatilization of organic acids from the samples.

The impact of neutralization of the autoclaved samples on the yield of glucose, xylose, arabinose, xylitol, glycerol and acetic acid was assessed by neutralization of all autoclaved hydrolysates with KOH to a pH value of 5; the results are indicated in Table 4.2. Knowledge on the inhibitory compounds can provide strategies towards efficient fermentation processes. The degradation products formed by pre-treatment of lignocellulose depend on both the biomass and the pretreatment conditions such as temperature, time, pressure, pH, redox conditions, and the addition of catalysts (Klinke et al., 2004). Knowing about the formation of by-products from lignocellulosic material is beneficial when the decomposed lignocellulose is used in a fermentation process. The study of van der Pol et al. (2014) indicated that the by-products can result in problems further downstream, since they can inhibit the growth and production of micro-organisms during fermentation. In this regard, Taherzadeh et al. (1997) reported that for fermentations at low pH, 3.5 g/l of acetic acid can reduce growth rates by 33% in *S. cerevisiae*, while at higher pH 9 g/l of acetic acid has the same effect.

Table 4.2. Mean results of neutralization of the hydrolysate with KOH to pH 5 and the concentration of hydrolyzed samples.

% H_2SO_4 used	Sample ID	Solid: Liquid ratio	Glucose (g/L)	Xylose (g/L)	Arabinose (g/L)	Xylitol (g/L)	Glycerol (g/L)	Acetic acid (g/L)
1%	B1	1:4	0.43 (0.01)	0.28 (0.00)	3.11 (0.25)	0.00	0.17 (0.03)	0.48 (0.06)
2%	C1	1:4	1.03 (0.00)	4.39 (0.05)	5.96 (0.61)	0.00	0.23 (0.02)	1.26 (0.11)
3%	D1	1:4	2.12 (0.40)	10.50 (1.89)	6.32 (1.37)	0.00	0.25 (0.01)	1.94 (0.50)
4%	E1	1:4	2.56 (0.22)	12.56 (2.14)	6.18 (1.63)	0.20 (0.00)	0.24 (0.00)	2.36 (0.15)
5%	F1	1:4	3.00 (0.42)	13.17 (1.76)	6.08 (1.59)	0.24 (0.02)	0.26 (0.01)	2.48 (0.53)
10%	G1	1:4	3.80 (0.75)	12.65 (2.82)	5.10 (0.62)	0.28 (0.00)	0.38 (0.04)	3.09 (0.17)
1%	B2	1:2	0.77 (0.09)	1.73 (0.60)	1.08 (0.04)	0.00)	0.27 (0.03)	0.26 (0.11)
2%	C2	1:2	1.18 (0.32)	3.62 (0.70)	9.86 (1.69)	0.00	0.34 (0.05)	1.81 (0.67)
3%	D2	1:2	2.22 (0.40)	11.20 (1.52)	10.86 (1.53)	0.00	0.40 (0.06)	2.61 (0.44)
4%	E2	1:2	3.97 (0.15)	18.76 (2.11)	11.03 (1.70)	0.00	0.40 (0.00)	3.40 (0.72)
5%	F2	1:2	4.37 (0.20)	21.80 (2.35)	11.12 (0.86)	0.00	0.40 (0.05)	3.83 (0.45)
10%	G2	1:2	5.93 (0.38)	22.67 (3.55)	9.86 (1.85)	0.00	0.49 (0.07)	4.34 (0.25)

* Values outside of the bracket are the mean results and those in brackets are the standard deviation values

The results in Table 4.2 indicate that, in general, while the samples are neutralized with KOH, it is observed that the amount of glucose, xylose, arabinose, xylitol, glycerol and acetic acid increases following the increase of H_2SO_4 used.

For solutions mixed in a 1:4 solid: liquid mixing ratio, changing the pH of autoclaved samples (Table 6.1) to 5 (Table 6.2), incremented the glucose and xylose concentration by 10% and 12%, respectively; this was observed for solutions mixed in 1% H_2SO_4. For the remaining solutions (2%, 3%, 4%, 5%, and 10% H_2SO_4), the yield of glucose was reduced by 1%, 5.8%, 7.3%, 4.8%, and 8.4%, respectively. Xiang et al. (2003) indicated that the disappearance of glucose during acid hydrolysis of lignocellulosic biomass was due to a recombination of glucose with acid soluble lignin in hydrolysates. The xylose concentration was also reduced. The arabinose yield was found to increase only for solutions treated with 1%, 2%, and 3%, and decreases for the other solutions (4%, 5%, and 10%). Furthermore, for solutions mixed in a 1:2 ratio, changing the pH of autoclaved samples (Table 6.1) to pH 5 (Table 6.2), led to an increment of the glucose concentration by 5.5%, 5.4% and 8.3% for solutions mixed in 1%, 2% and 3% H_2SO_4, respectively. For the remaining solutions (4%, 5%, and 10% H_2SO_4), the yield of glucose concentration was reduced by 4.3%, 2.9%, and 6.3%, respectively.

In order to explain these results, the comprehensive kinetic model prepared for dilute-acid hydrolysis of cellulose by Xiang et al. (2003) indicated that once the crystalline structure of the cellulose is disrupted, acid molecules can penetrate into the inner layers of the cellulose chains, and once glucose is formed in the hydrolysate, it interacts with acid-soluble lignin, forming a lignin-carbohydrate complex at further treatment. Moreover, the study by Woldesenbet et al. (2014) on hydrolysis of wet coffee pulp and mucilage using different concentrations of H_2SO_4 (0%, 1%, 2%, 3% and 4%) reported that the total reducing sugar content increases with an increase in acid concentration up to 3%, and then decreases. Davis et al. (2005) also analyzed the concentration of the release of sugars from wheat stillage cellulose and hemicelluloses using (0–4% (v/v)) of H_2SO_4, and found that sugar recovery from both hemicellulose and cellulose peaked at 2% H_2SO_4. The study conducted by Urbaneja et al. (1996) on oven dried coffee pulp from Venezuela using diluted H_2SO_4 (0.5, 1, 1.5 and 2 %) also reported that the glucose yield increased with higher acid concentration and the greatest yield was obtained at 2.0% H_2SO_4.

In fact, with 10 % H_2SO_4 a better sugar yield could be obtained. However, the concentration of acetic acid, which is inhibitory for fermentation, would simultaneously increase. Thus, mild conditions of H_2SO_4, i.e., 3 % H_2SO_4, are a better choice. Different studies also support using 3% H_2SO_4. On the other hand, glycerol generation is decreasing in both 1:2 and 1:4 mixing ratios after neutralization. This implies that varying the pH of the hydrolysate could affect the solubilization of sugars and byproducts during the pretreatment. Therefore, to proceed with the investigation under optimum conditions depending on the obtained results, the sample was treated with 3 % (v/v) H_2SO_4 in a solid to liquid ratio of 1:4 for baker's yeast and 1:2 for lignocellulosic yeast.

4.3.4 Fermentation of dried coffee pulp with baker's yeast

First, different conditions were evaluated using baker's yeast to ferment the coffee sample in order to obtain optimum ethanol yield. For this purpose, the sample was fermented for 48 h and samples were taken every 6 h. Thus, the optimal ethanol yield was obtained after 6 h of fermentation. The ethanol titer obtained was 1.92 ± 0.4 g/L. At the end of the fermentation (6 h), the yield of glucose, xylose, arabinose, xylitol, glycerol, and acetic acid in the hydrolysate was measured; this is shown in Table 4.3. According to the study of van Maris et al. (2006) on plant biomass hydrolysates, it was indicated that the pentose sugar xylose ('wood sugar') is the major monosaccharide that cannot be fermented by wild-type strains of S. *cerevisiae*. This is the reason why xylose, with a concentration of 9.19 ± 0.85 and 5.69 ± 0.50 g/L of arabinose is left in the hydrolysate without being used by the yeast (see Table 4.3).

Table 4.3. Mean results of initial concentration of hydrolysates and their concentration in fermented broths

Concentration (g/L)	**Yeast**											
	Baker's						**C5**					
	Glucose	Xylose	Arabinose	Xylitol	Glycerol	Acetic acid	Glucose	Xylose	Arabinose	Xylitol	Glycerol	Acetic acid
Initial conc. of autoclaved and neutralized hydrolysate	2.12 (0.40)	10.50 (1.89)	6.32 (1.37)	0.00	0.25 (0.01)	1.94 (0.50)	2.22 (0.40)	11.20 (1.52)	10.86 (1.53)	0.00	0.40 (0.06)	2.61 (0.44)
Optimum conc. using enzymatic hydrolysis	*	*	*	*	*	*	6.84 (2.87)	11.41 (1.78)	10.92 (0.62)	0.75 (0.16)	0.48 (0.19)	2.62 (0.32)
Conc. at the optimum fermentation time	0.25 (0.01)	9.19 (0.85)	5.69 (0.50)	0.62 (0.16)	0.38 (0.02)	1.90 (0.19)	0.31 (0.02)	1.89 (1.07)	5.24 (0.78)	0.59 (0.06)	1.67 (0.11)	2.82 (0.46)

* No enzymatic hydrolysis

* Values outside of the bracket are the mean results and those in brackets are the standard deviation values

Similarly, different conditions using cellulolytic enzymes accellerase® TRIO™ for hydrolysis and lignocellulosic yeast GSE16-T18 for fermentation were evaluated to select the optimum conditions. Using this enzyme, the optimal hydrolysis time was found to be 48 h. At this hydrolysis time, the yield of glucose, xylose, arabinose, xylitol, glycerol, and acetic acid in the hydrolysate is as shown in Table 4.3. The results indicate that the enzyme hydrolysis enhanced the glucose yield at least by a factor 3 (relative to the glucose concentration from hydrolysate after 3% H_2SO_4 treatment). Subsequently, the hydrolysates were fermented for 48 h and samples were taken every 6 h. The optimum ethanol yield (7.03 ± 2.63 g/L) was obtained after 12 h of fermentation. The results are indicated in figure 4.1.

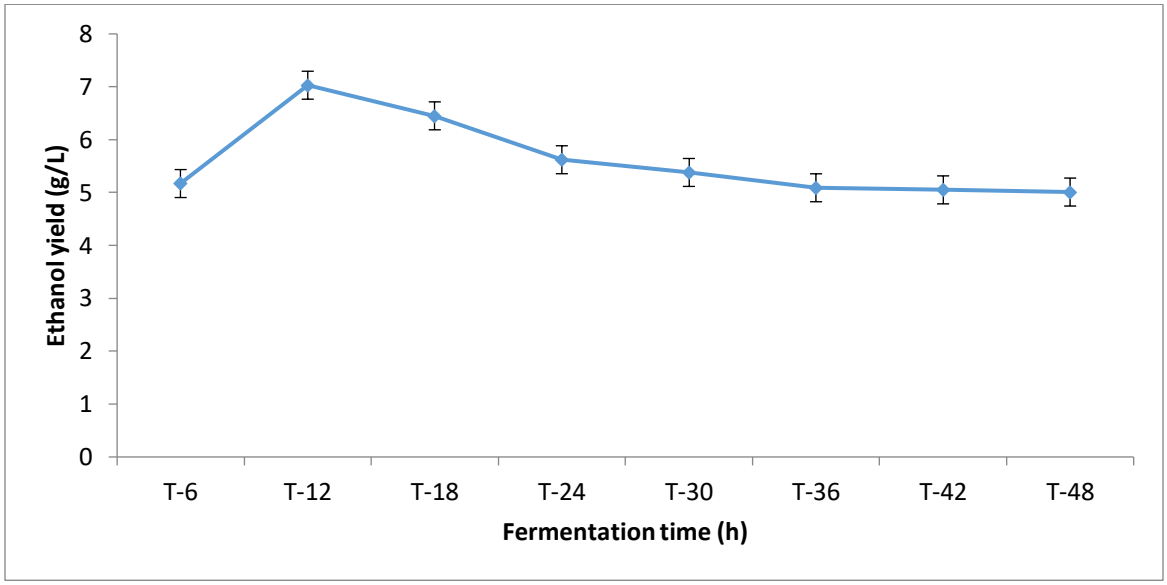


Fig. 4.1 Variation of ethanol yield with fermentation time (using C5 yeast).

As shown in figure 4.1, after the optimum ethanol concentration (7.03 ± 2.63 g/L) was obtained, the ethanol concentration was found to slightly decrease with time. This might be because the yeasts are shifting to use ethanol as the source of carbon. Another reason might be that ethanol is a poison for the yeast. In this regard, Birch and Walker (2000) indicated that ethanol is an inhibitor of yeast growth at relatively low concentrations, inhibiting cell division, decreasing cell volume and specific growth rate, while high ethanol concentrations reduce cell

vitality and increase cell death. Therefore, it is crucial to continuously remove ethanol from the broth. At the end of the optimum fermentation time (12 h), the yield of glucose, xylose, arabinose, xylitol, glycerol, and acetic acid in the hydrolysate was 0.31 ± 0.00, 1.89 ± 1.07, 5.24 ± 0.78, 0.59 ± 0.06, 1.67 ± 0.11 and 2.82 ± 0.46 g/l, respectively (Table 4.3). These figures indicate that arabinose was barely consumed by the GSE16-T18 yeast.

These results are in agreement with the earlier studies by Demeke et al. (2013a) and (2013b), which confirmed that the yeast GSE16-T18 strain contains a heterologous pathway for arabinose fermentation, but it still has poor functionality. This is the reason why 5.24 ± 0.78 g/L of arabinose is remaining at the optimum fermentation time without being consumed by the yeast (see Table 4.3). Hence, by using the lignocellulosic yeast GSE16-T18, the bioethanol yield increased by a factor of about 4 compared to that obtained with baker's yeast. Soares et al. (2016) reported that using the same yeast GSE16-T18, it was possible to obtain a maximum ethanol concentration of 3.73 ± 0.2 % (v/v) from coconut mesocarp husk. Table 4.3 indicates the initial concentration of autoclaved and neutralized hydrolysates, the optimum concentration using enzymatic hydrolysis as well as the concentration of fermented broths at the optimum fermentation time.

A comparison of the results from this study demonstrates that dried coffee pulp can be used as an alternative substrate for ethanol production, in comparison to different biomass resources as shown in Table 4.4.

Table 4.4. Comparison of ethanol yields of various substrates as reported in the literature with the results obtained in the present study.

Residue	**Ethanol Yield (g/L)**	**Reference**
Corn stalks (using lime treatment, enzyme hydrolysis, *Saccharomyces* cerevisiae and Pachysolen tannophilus ATCC 32691)	5	Belkacemi et al. (2002)
Barley straw (using lime treatment, enzyme hydrolysis, *Saccharomyces* cerevisiae and Pachysolen tannophilus ATCC 32691)	10	Belkacemi et al. (2002)

Wheat stillage (using 2% H_2SO_4 (v/v), enzyme hydrolysis and *Zymomonas* mobilis ZM4(pZB5))	11	Davis et al. (2005)
Coffee residue waste (using popping pretreatment, enzymatic hydrolysis, *Saccharomyces* cerevisiae)	15.3	Choi et al. (2012)
Sweet sorghum bagasse (using steam explosion pretreatment, enzyme hydrolysis, and *Saccharomyces* cerevisiae)	16.2	Ballesteros et al. (2004)
Corn Stover (using steam pretreatment, enzyme hydrolysis, and *Saccharomyces* cerevisiae)	16.8	Öhgren et al. (2007)
Eucalyptus (using steam explosion pretreatment, enzyme hydrolysis, and *Saccharomyces* cerevisiae)	17	Ballesteros et al. (2004)
Wheat straw(using steam explosion pretreatment, enzyme hydrolysis, and *Saccharomyces* cerevisiae)	18.1	Ballesteros et al. (2004)
Poplar (using steam explosion pretreatment, enzyme hydrolysis, and *Saccharomyces* cerevisiae)	19	Ballesteros et al. (2004)
B.Carinata residue(using steam explosion pretreatment, enzyme hydrolysis, and *Saccharomyces* cerevisiae)	19	Ballesteros et al. (2004)
Dried coffee pulp hydrolysis with cellulolytic enzymes and fermentation with lignocellulosic yeast GSE16-T18	7.03 ± 2.63	This study

4.3.5 Ethanol pervaporation of the fermented waste fraction

4.3.5.1 Pervaporation of dried coffee pulp fermentation with baker's yeast

The fermented broth having a total volume of 1.2 L and containing glucose (0.25 ± 0.00), xylose (9.19 ± 0.85), arabinose (5.69 ± 0.50), xylitol (0.62 ± 0.16) , glycerol (0.38 ± 0.02), acetic acid (1.90 ± 0.19) and ethanol (1.92 ± 0.40) g/L was filtered and pervaporated at different temperatures (30, 40, 50 and 60 °C). The concentration of xylitol, glycerol and acetic acid in the

permeate was 0.03 ± 0.00, 0.02 ± 0.00 and 0.24 ± 0.11 g/L respectively. The pervaporation results are shown in Table 4.5.

Table 4.5. Permeate levels obtained after pervaporation of dried coffee pulp fermentations with baker's yeast.

IC (feed solution) (g/L ethanol)	**Pervaporation temperature (°C)**	**Pervaporation pressure (mbar)**	**Ethanol concentration (g/L) in the permeate**
1.92 ± 0.40	30	13.80	2.56 ± 0.20
	40	14.77	3.33 ± 0.30
	50	15.56	3.40 ± 0.80
	60	15.15	4.06 ± 0.01

IC = initial concentration

As shown in figure 4.2a and 4.2b, the membrane flux increases with temperature. Increasing the temperature typically produces an increase of the total and individual solute fluxes through the membrane due to the increase in vapor pressure and consequent increase in the driving force (Luis et al., 2013; Chovau et al., 2011). The membrane flux with pervaporation temperature is indicated in figure 4.2a-b. The feed ethanol solution concentration was 1.92 ± 0.4 g/L (Table 4.5). In addition, the maximum level of ethanol obtained from the pervaporation of coffee pulp using baker's yeast was 4.06 ± 0.01 g/L. Thus, the bioethanol concentration obtained is doubled due to the pervaporation.

4.3.5.2 Pervaporation of dried coffee pulp fermentation with lignocellulosic yeast GSE16-T18

The coffee pulp samples were also hydrolyzed with the cellulolytic enzymes and fermented with the lignocellulosic yeast GSE16-T18. The fermented broth containing glucose (0.31 ± 0.00), xylose (1.89 ± 1.07), arabinose (5.24 ± 0.77), xylitol (0.59 ± 0.06), glycerol (1.67 ± 0.11), acetic acid (2.82 ± 0.46) and ethanol (7.03 ± 2.63) g/L was filtered and pervaporated at different temperatures (30, 40, 50 and 60 °C). The concentration of xylitol, glycerol and acetic

acid in the permeate was 0.01 ± 0.00, 0.01 ± 0.00 and 0.03 ± 0.00 g/L, respectively. The results are shown in Table 4.6.

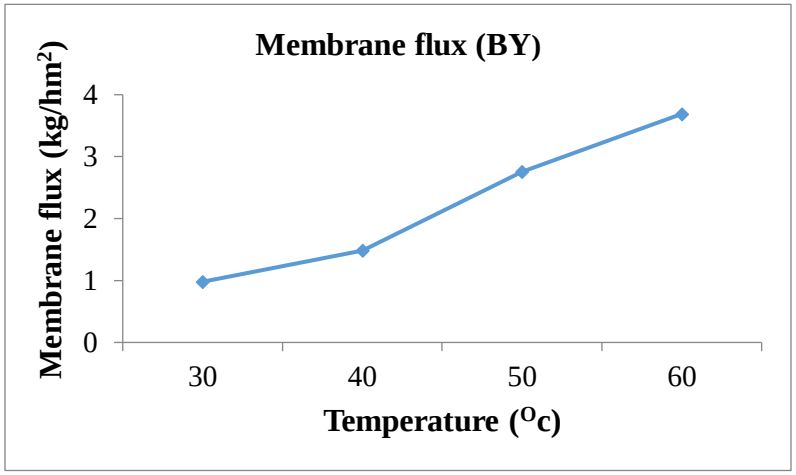
Table 4.6. Permeate levels obtained after pervaporation of dried coffee pulp hydrolyzed with cellulolytic enzyme and fermented with lignocellulosic yeast GSE16-T18.

IC (feed solution) (g/L ethanol)	**Pervaporation temperature (°C)**	**Pervaporation pressure (mbar)**	**Ethanol concentration (g/L) in the permeate**
7.03 ± 2.63	30	16.75	9.10 ± 1.48
	40	12.25	9.45 ± 0.28
	50	10.75	15.47 ± 0.66
	60	10.50	13.04 ± 1.55

IC = initial concentration

The feed ethanol solution concentration was 7.03 ± 2.63 g/L. The maximum concentration of ethanol obtained by pervaporation was 15.47 ± 0.66 g/L and this was obtained with pervaporation of the sample at 50 °C. This shows that a much better ethanol yield from coffee pulp samples was obtained when using cellulolytic enzyme (accellerase) and lignocellulosic yeast compared to using only baker's yeast. The maximum ethanol concentration produced after pervaporation of the sample was found to be 15.47 ± 0.66 g/L. Hence, it was observed that the bioethanol concentration is more than double after using pervaporation.

The pervaporation performance of membrane is indicated in figures 4.2a-j. In general, the membrane flux and water/ethanol separation factor were found to increase with increasing pervaporation temperature using both yeasts.



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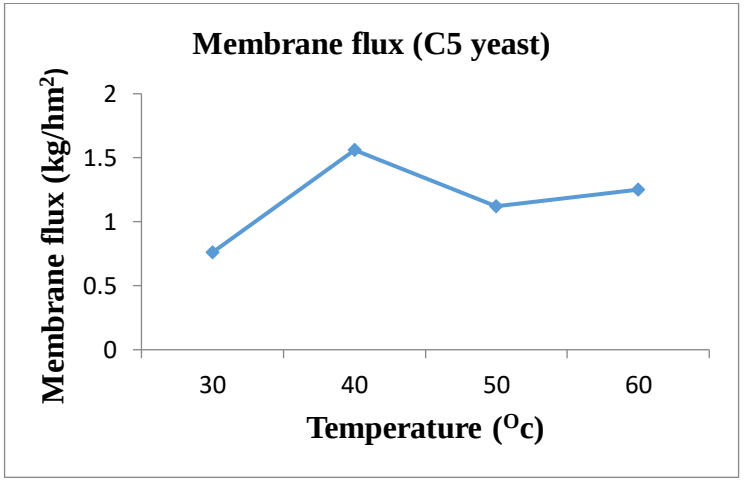

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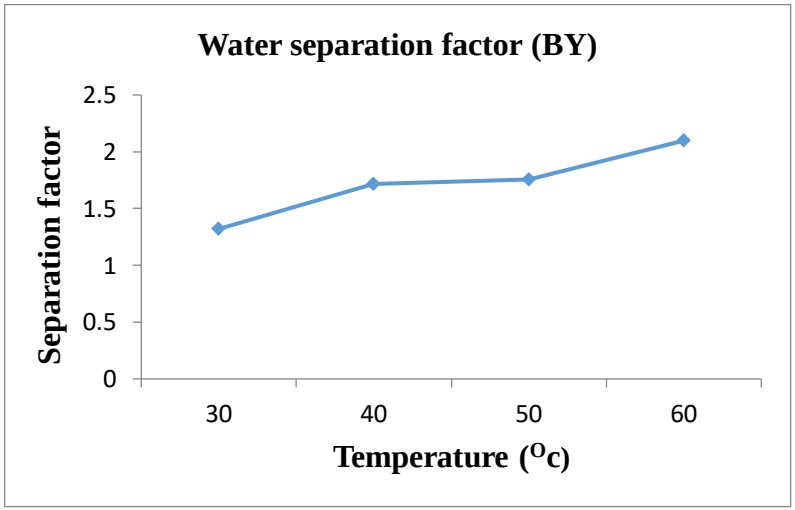

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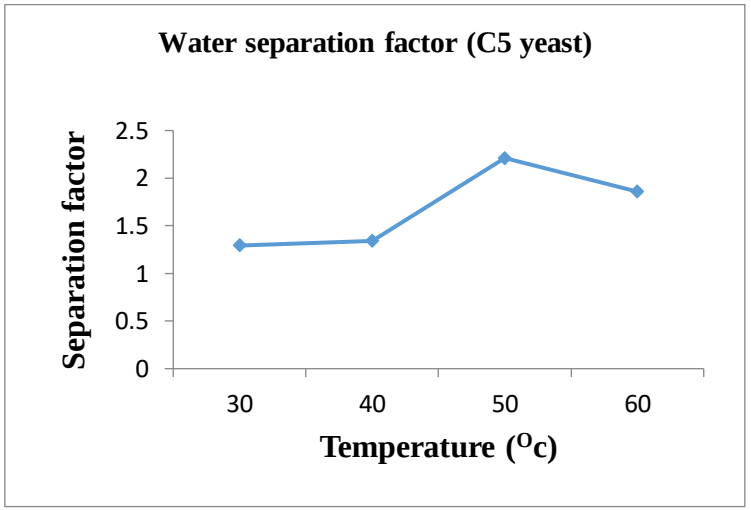

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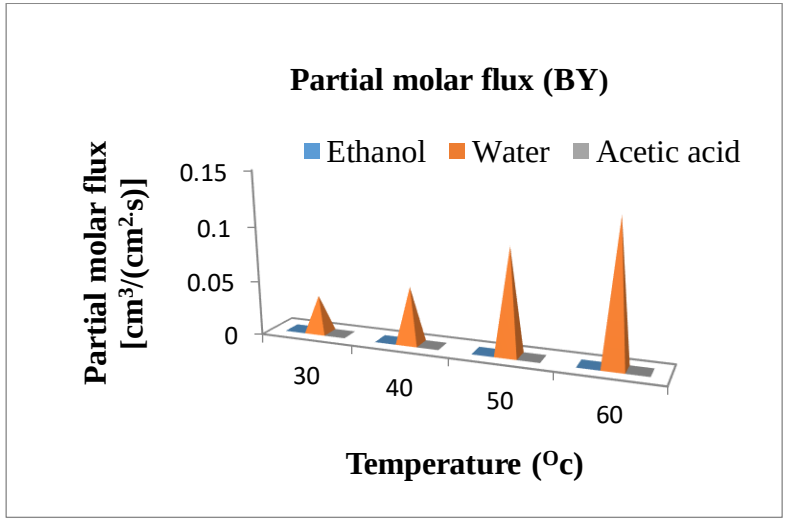

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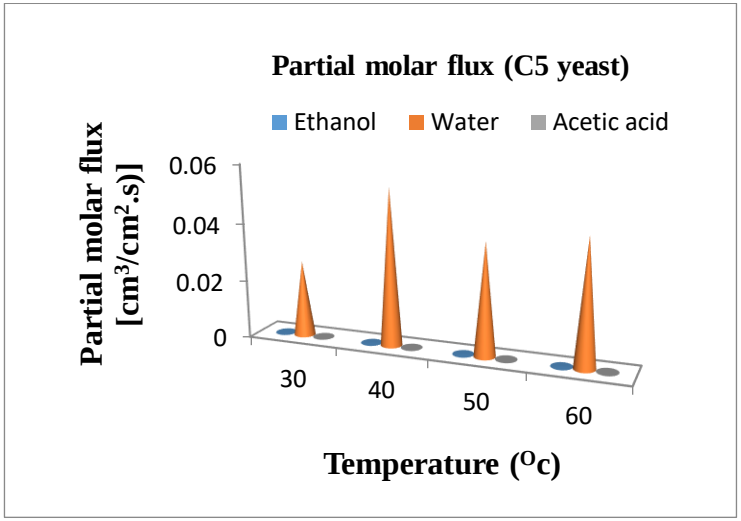

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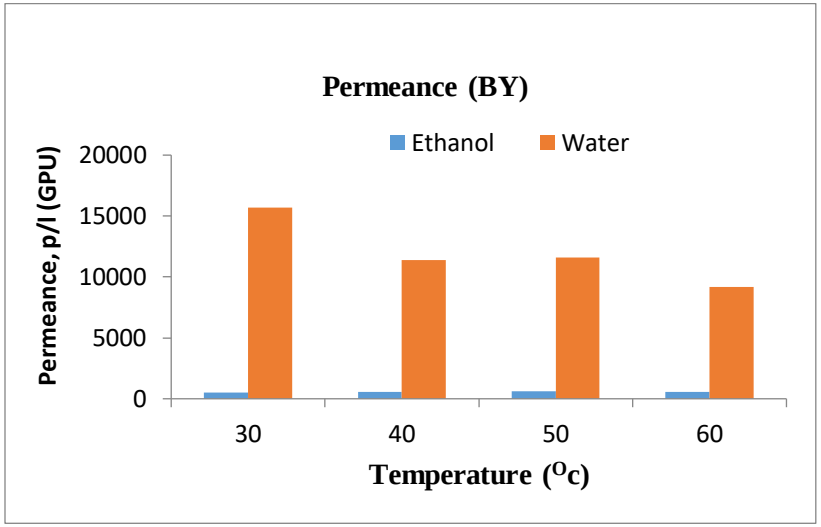

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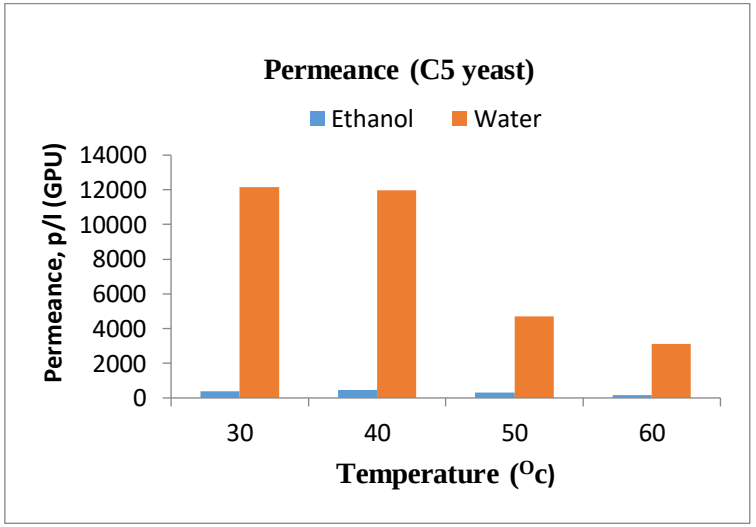
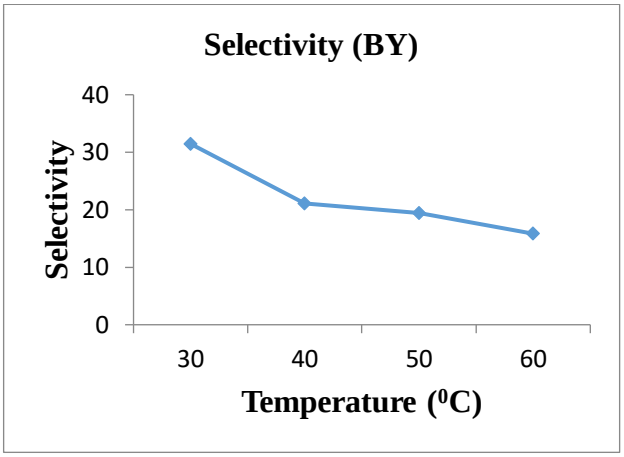
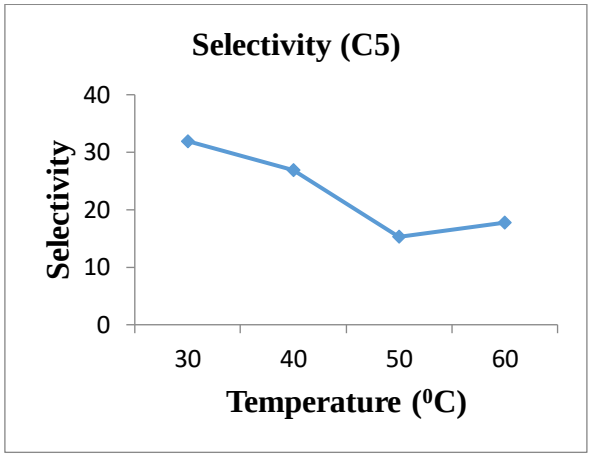


4.2h





4.2i 4.2j

*BY = baker's yeast

Fig. 4.2. Variation of membrane flux, water/ethanol separation factor, partial molar flux, permeance, and water/ethanol selectivity using baker's (BY) and lignocellulosic yeast (C5).

As indicated above, the water separation factor is below 3, and in general, the values were found to increase with increasing pervaporation temperature. The water/ethanol selectivity is calculated to be greater than 15 in both cases (using baker's yeast and lignocellulosic yeast, C5). Besides, as indicated in Figures 4.2e-h, for both yeasts, the partial molar flux and permeance of water are higher than for ethanol.

The study conducted by Shenoy et al. (2011) on dried coffee pulp reported that the theoretical ethanol yield that could be obtained from the dried coffee pulp is 9.35 %. Similarly, Choi et al. (2012) performed enzymatic hydrolysis (after simultaneous saccharification and fermentation) obtaining an ethanol concentration of 15.3 g/L from coffee residue waste. In the study of Davis et al. (2005) on wheat stillage hydrolysate fermentation supplemented with glucose 10 g/L by recombinant Zymomonas mobilis ZM4(pZB5), the possibility of producing 11 g/L ethanol was reported.

In general, this study indicates that the production of ethanol via hydrolysis with cellulolytic enzymes, fermentation with lignocellulosic yeast, and then pervaporation of dried coffee pulp (15.47 ± 0.66 g/L) was satisfactory in comparison with literature data for other

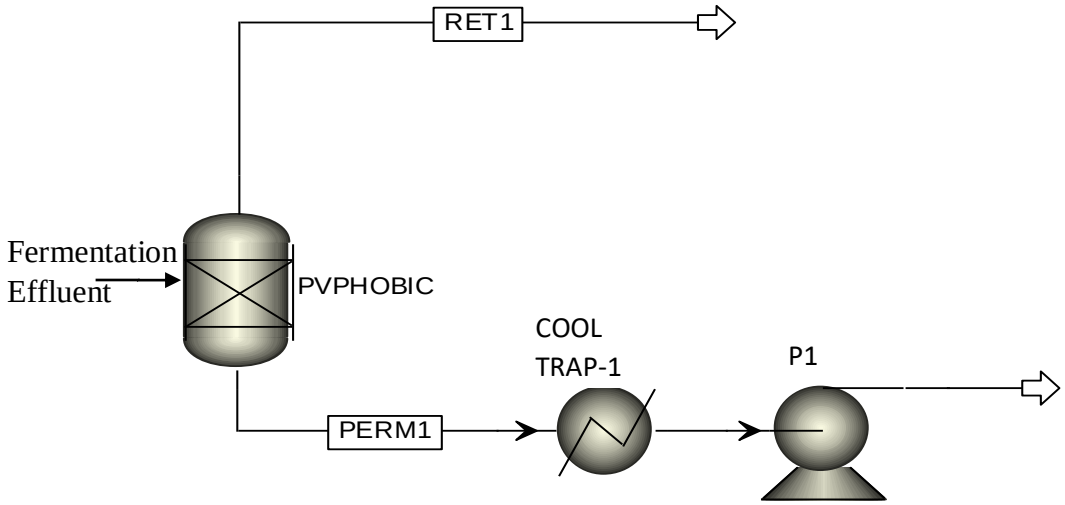
substrates: corn stakes (5 g/L); barley straw (10 g/L); wheat stillage (11 g/L); and coffee residue waste (15.3 g/L) as indicated in Table 4.4.

Even though the manufacturer indicates that the membrane is alcohol selective, the results show the difficulty to reach a high concentration of ethanol (since the ethanol/water separation factor and permeance of the membrane were too low, while the ethanol selectivity is even below 1, indicating the ability of separation of water as indicated above in figure 4.2) with polyvinyl alcohol type M1 pervaporation membrane. In the following section, the performance of real membranes used in other reported studies is shown and compared in terms of energy requirements.

4.3.6 Simulation of alternative systems for bioethanol production

Simulations of both alternatives (hydrophobic and hydrophilic membrane) have been performed in Aspen Plus to further estimate the potential of pervaporation. The energy requirements were calculated to make a comparison between different options. Figure 4.3 depicts the hydrophobic and hydrophilic membrane alternative mode of pervaporation unit energy requirements.

4.3a)



4.3b)

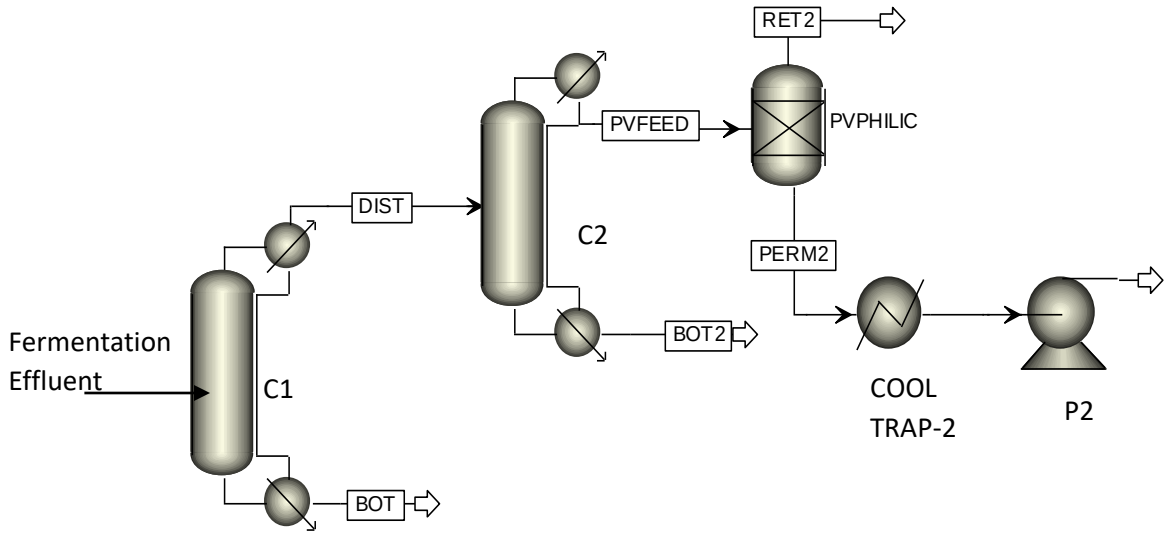


Fig. 4.3. a) Hydrophobic membrane alternative mode of pervaporation unit, PVPHOBIC (Hydrophobic membrane alternative mode of pervaporation unit); heat exchange, COOL TRAP-1; centrifugal pump, P1.

b) Hydrophilic membrane alternative made of: stripper, C1; distillation column, C2; pervaporation unit, PVPHILIC (Hydrophilic membrane alternative mode of pervaporation unit); heat exchange, COOL TRAP-2; centrifugal pump, P2.

Figure 4.3a depicts a case in which a hydrophobic membrane is applied, as described above. The membrane unit (PVPHOBIC) separates the mixture into two streams: a permeate rich in ethanol (PERM1) and a retentate (RET1) rich in water with other compounds present in the upstream mixture. The permeate stream is sent to a cooler (COOL TRAP-1) followed by a centrifugal pump (P1) to transport the fluid (steam) at ambient condition.

In case of figure 4.3b, the fermentation products are sent to a stripper column (C1) that evaporates all the ethanol and part of the water. Then the distillate stream is sent to a distillation column (C2): at the bottom stream almost pure water is present, while the distillate stream has a composition close to the azeotrope (91.3 wt% ethanol). The latter stream is sent to a pervaporation unit (PVPHILIC), this time water selective, in which the permeate is rich in water (PERM2) while the retentate is rich in ethanol (RET2).

A sensitivity analysis was carried out for figures 4.3a and b, to investigate the effect of the separation factor on the energy requirements per unit of permeate amount and on the purity of the components in their relative product streams. This analysis was carried out following the approach by Luis et al. (2014). In particular, two different membrane performances have been considered for each alternative reported in figure 4.3:

I) A membrane that achieves that 99.9% of the unlike-affinity components arriving at the pervaporation unit is kept as retentate and almost pure like-affinity component permeates (i.e., low flux and high separation factor); and

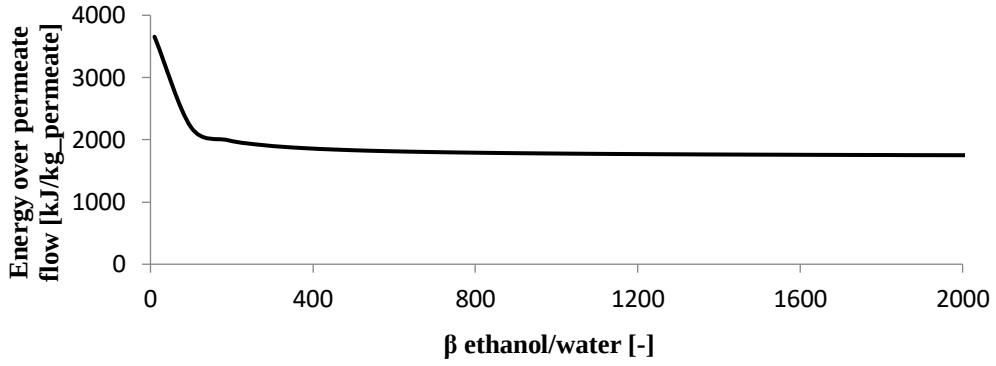
II) A membrane in which 95% of the component that arrives at the pervaporation unit like-affinity component but a pure permeate could not be achieved (i.e., higher flux but low separation factor).

The case in which a hydrophobic membrane is considered is indicated in the figures 4.4a-d. For the hydrophobic membrane alternative (figure 4.3a), the like affinity component

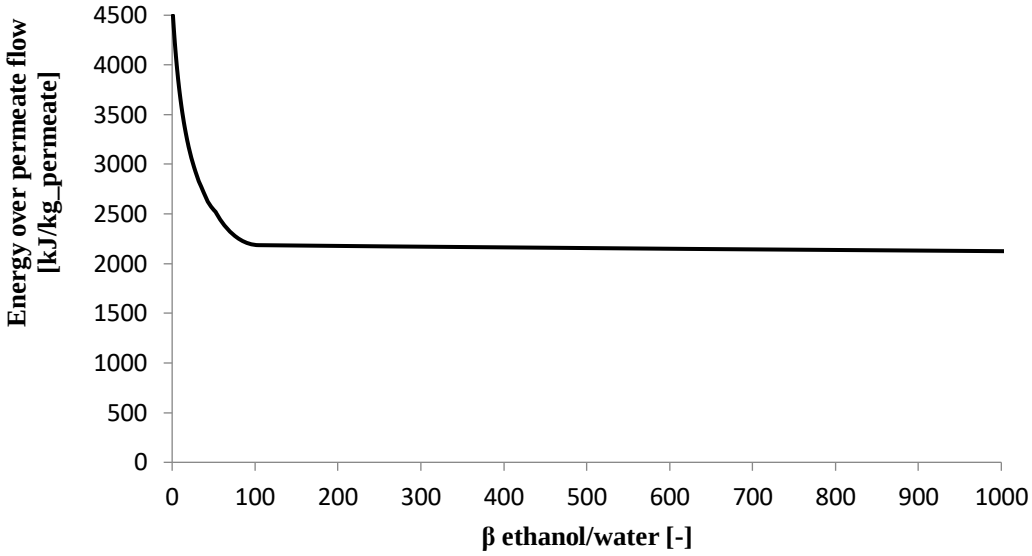
is ethanol and water is the unlike-affinity, while for the hydrophilic membrane case (figure 4.3b) it is the opposite. In the energy calculations per unit of permeate flow, the two alternatives (hydrophobic and hydrophilic membranes) are taken into account.

Figure 4.4a reports the results of the case with a hydrophobic membrane (99.9% of the unlike-affinity component, which is Alternative I). The energy per unit of permeate flow has the same trend in both cases (Figure 4.4a and Figure 4.4b). It decreases at low values of the separation factor, then becomes constant for values higher than 100. The only difference is that the values of energy per unit of permeate for the case with low separation factor (Figure 4.4b) (95% of the component that arrives at the pervaporation unit is like-affinity component, which is alternative II) are higher than the other case because the amount of permeate (all the ethanol with a part of water) is higher so the energy required increases.

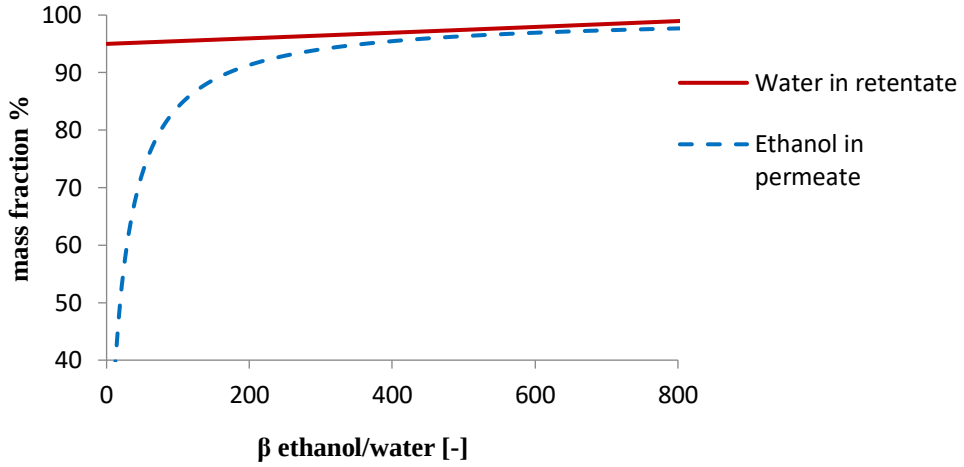
4.4a)



4.4b)


Energy over permeate flow [kJ/kg_permeate]
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
100
200
300
400
500
600
700
800
900
1000
β ethanol/water [-]

4.4c)


mass fraction %
100
90
80
70
60
50
40
0
200
400
600
800
β ethanol/water [-]
Water in retentate
Ethanol in permeate

4.4d)

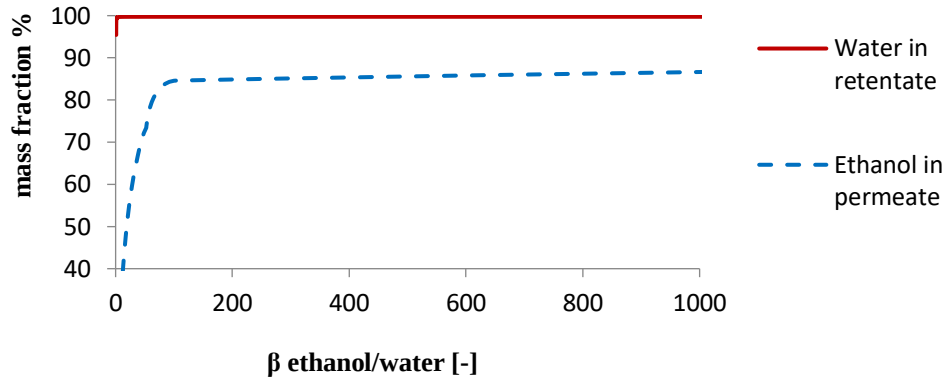


Fig. 4.4. Hydrophobic membrane:

A. Energy requirements for mass of permeate of high selective with low flux membrane;
B. Energy requirements for mass of permeate of low selective with high flux membrane;
C. Purity of ethanol in permeate (PERM1) blue dotted line and water (RET1) red full line of high selective with low flux membrane;
D. Purity of ethanol in permeate (PERM1) blue dotted line and water (RET1) red full line of low selective with high flux membrane.

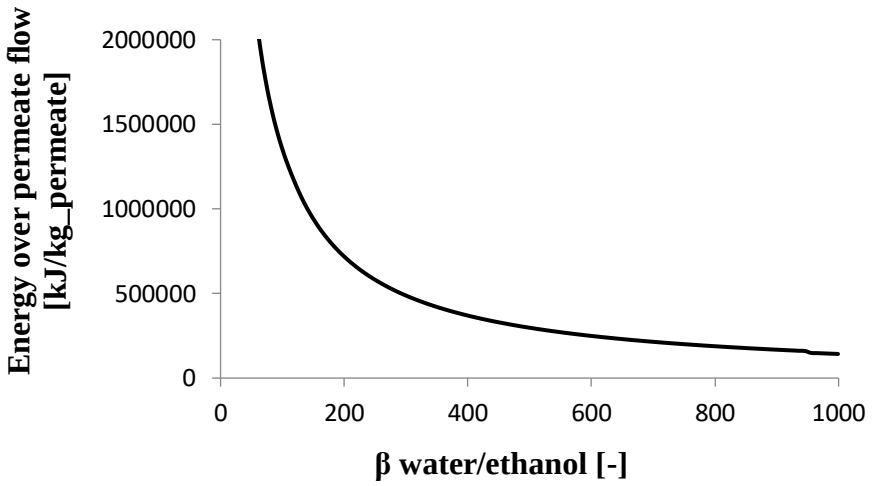
The purity of the two compounds, in the retentate for water (RET1) and in the permeate for ethanol (PERM1), is achieved only for the case with a highly selective membrane (Figure 4.4c), while for the case with a high flux membrane, figure 4.4d, there is a limit to the ethanol purity.

The case in which a hydrophilic membrane is considered is indicated in the figures 4.5a-d. It has to be mentioned that in the calculation of energy consumption per unit of permeate, the energy consumed by the stripper (C1) and the distillation column (C2) before the membrane (PVPHLIC) are also taken into account.

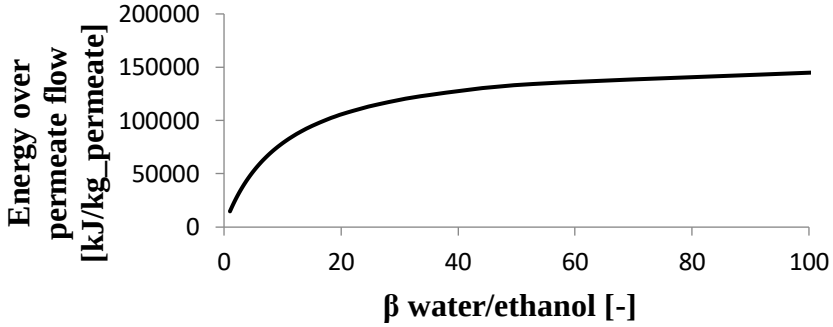
It appears that for this configuration for both cases of membrane performances (Figures 4.5a-b), the energy requirements are much higher than the case with hydrophobic membranes (Figures 4.4a-b). This large difference with the hydrophobic membrane is attributed to the presence of two distillation columns (stripper and distillation columns),

which consumes the majority of the total energy. Specifically, in the case with a highly selective membrane (Fig 4.5a) the energy requirements become constant after a separation factor of 800, while for the high flux membrane, once there is almost only water in the permeate, there is no more significant variation of energy per unit of permeate.

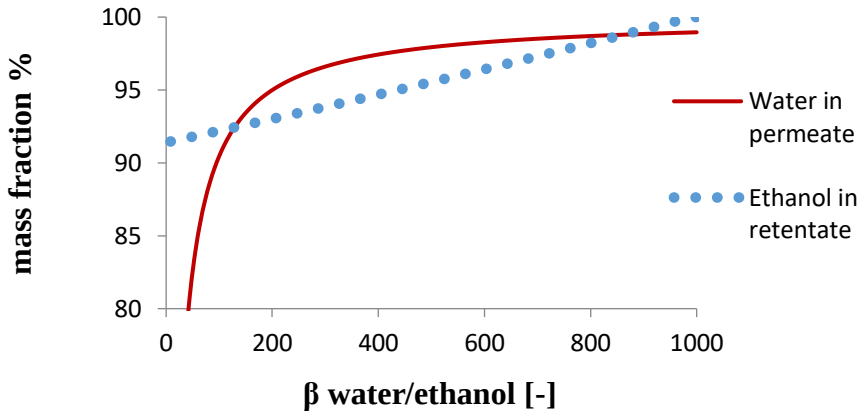
4.5a)



4.5b)



4.5c)



4.5d)

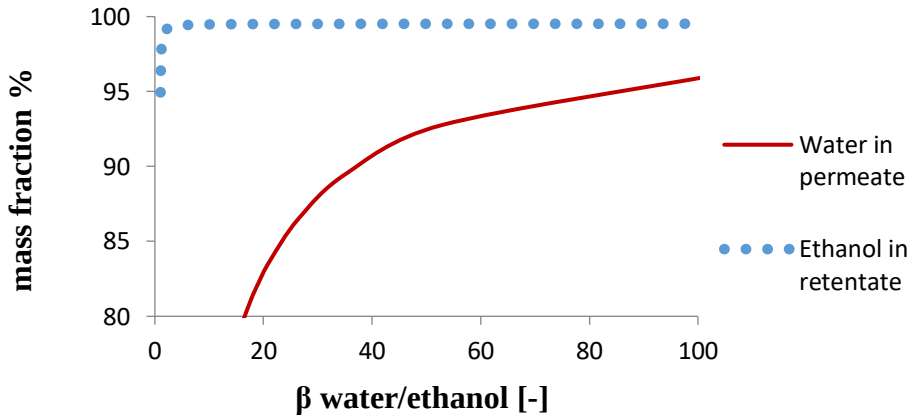


Fig. 4.5. Hydrophilic membrane:

A. Energy requirements for mass of permeate of high selective with low flux membrane;
B. Energy requirements for mass of permeate of low selective with high flux membrane;
C. Purity of ethanol in retentate (RET2) blue dotted line and water (PERM2) red full line of high selective with low flux membrane;
D. Purity of ethanol in retentate (RET2) blue dotted line and water (PERM2) red full line of low selective with high flux membrane.

Finally, the results in figure 4.5c-d are closely related to those of figure 4.4c-d, thus only for the highly selective membrane, both components are almost pure in their respective streams. The results show clearly that for this specific application the hydrophobic membrane

is the best choice in terms of energy consumptions due to the separation towards the component in a low amount in the fermenter effluent (i.e., ethanol).

Thus ideally, for this separation, the best choice is an alcohol selective membrane. The feasibility of this separation was verified using the separation factor of real membranes reported by other studies (Vane, 2006; Abels et al., 2013; Amelio et al., 2016). In particular, some of the best membranes found in the literature were simulated, using always the component splitter, to evaluate the current situation of hydrophilic and hydrophobic membranes (Mori and Inaba, 1990; Caro et al., 2000; Chanachai et al., 2000; Lin et al., 2003; Volkov et al., 2004; Huang et al., 2010). Figure 4.6 shows the maximum purity achieved in the permeate for both cases.

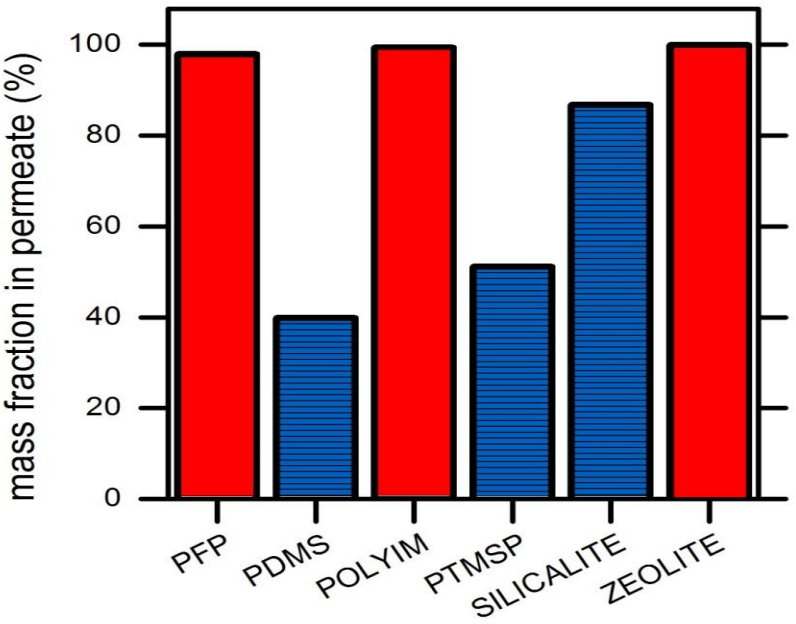


Fig. 4.6. Mass fraction in the permeate of water for full red color and ethanol with the blue horizontal pattern for different existing membranes (PFP: Perfluoropolymer; PDMS: Polydimethylsiloxane; PTMSP: Poly (1-trimethylsilyl-1-propyne); POLYIM: Polyimide).

It is clear that when the membrane is hydrophilic, for all cases a very high purity in the permeate is achieved so that a complete separation of the two component is successfully

achieved. On the other hand, for all the hydrophobic membranes, it is not possible to reach pure ethanol in the permeate. Thus, the current situation for real hydrophobic membranes is not very close to the ideal separation, and more research is needed to find a membrane suitable for this application, while for the hydrophilic ones even though detailed research is not needed, the research should focus on other parameters such as flux and permeability.

The energy consumption for these real membranes is reported in Figure 4.7. It has to be mentioned that the perfluoropolymer (PFP) membranes were applied in vapor permeation mode. The simulations show that for treating the same amount of the mixture (also for the real membranes), the hydrophobic membranes are the best option for energy requirements in particular for the silica, for which the value is very close to the ideal situation. Nevertheless, none of these real hydrophobic membranes is able to produce a stream containing pure ethanol, while the hydrophilic membranes have the same values to the ideal hydrophilic in both energy requirements and purities. Thus, for the hydrophilic membrane, it can be concluded that the limit is reached.

Finally, a third configuration using vapor permeation can be considered. This case is simulated in the same way as the hydrophilic pervaporation, figure 4.3b, since PFP is also a hydrophilic membrane, with the only difference that in the second distillation column of figure 4.3b there is partial condenser, instead of a total one, so the feed to the hydrophilic is a vapor, not a liquid (Huang et al., 2010). The results show that among the alternatives considered, vapor permeation is the best option, since it is able to achieve the maximum purity required, the main goal and the energy consumption is comparable to the hydrophobic case.

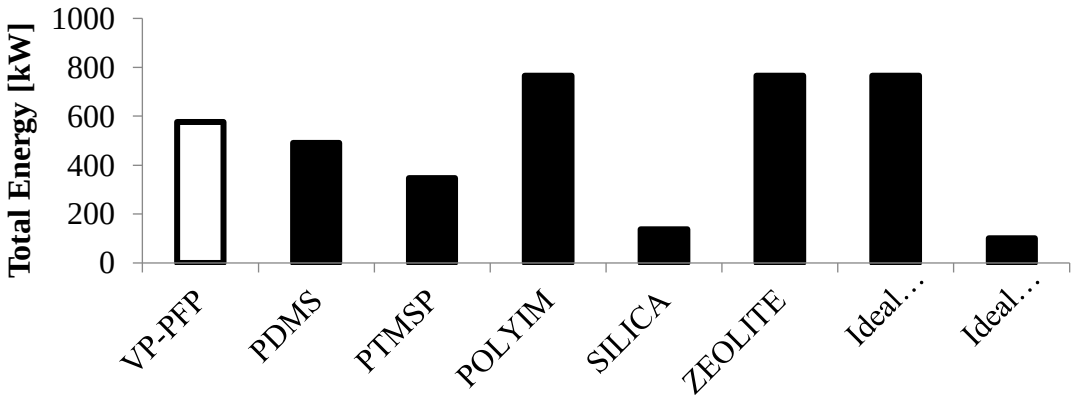


Fig. 4.7. Energy requirements of the different kind of existing membranes reported in the literature compared to the ideal cases (Mori and Inaba, 1990; Caro et al., 2000; Chanachai et al., 2000; Lin et al., 2003; Volkov et al., 2004; Huang et al., 2010). (VP-PFP: Vapor Permeation Perfluoropolymer; PDMS: Polydimethylsiloxane; PTMSP: Poly (1-trimethylsilyl-1-propyne); POLYIM: Polyimide).

4.4 Conclusions

Coffee pulp is discharged into water bodies and soil near wet coffee processing industries, which causes serious environmental and health concerns. To address this problem, the potential of dried coffee pulp for bioethanol using the lignocellulosic yeast GSE16-T18 for fermentation and its purification by pervaporation was investigated. Even though the yield of fermentable sugar is increasing as the amount of diluted sulfuric acid is increasing, this increment of acid (diluted sulfuric acid) also increases the concentration of unwanted byproducts such as acetic acid, xylitol, and glycerol. Thus, to obtain an optimum reducing sugar concentration, the final experiment was conducted only with 3% sulfuric acid. The optimization study indicates that 48 enzyme hydrolysis and 12 h fermentation of the samples with lignocellulosic yeast GSE16-T18 strain is the best fermentation times at which better ethanol titer (7.03 ± 2.63 g/L) were obtained. Pervaporation of the fermented feed concentrated the ethanol to 15.47 ± 0.66 g/l. This indicates that hydrophobic pervaporation is not sufficient to adequately purify ethanol. This is because at the start the concentration of

ethanol in the feed solution is low and the membrane used should be ethanol selective; such membranes have a too low selectivity. Alternatives such as combinations of hydrophobic pervaporation - hydrophilic pervaporation, and then as a third option, distillation (as in a classical process) followed by pervaporation dehydration should be considered, which yields a sufficient purity of ethanol. The simulation results showed that hydrophobic pervaporation is theoretically the best option (in terms of energy), but at present, a complete separation can be only achieved with the hydrophilic membranes combined with distillation in the hybrid configuration. For this last kind of membrane, a further saving of energy can be achieved by working in vapor permeation mode. The hydrolysis results indicate that the hydrolysate is composed of more of xylose and arabinose than glucose. Therefore, to produce more ethanol, future studies should focus on strains that can utilize arabinose effectively.

5. Composting and co-composting of coffee husk and pulp with source separated municipal solid waste: a breakthrough in valorization of coffee waste

Abstract

Composting is considered one of the most suitable methods used for sustainable processing of organic waste materials. In this chapter, the composting and co-composting potential of coffee husk and pulp with source separated municipal solid waste (SSMSW) was investigated. Coffee husk and pulp were mixed independently with SSMSW in different proportions (0, 33, 50 and 100%), and composted in triplicates with a total of 24 composting piles for 3 months. The aerobic windrow composting method was applied. From each compost type different physicochemical parameters (pH, electrical conductivity, organic carbon, organic matter, total nitrogen, available phosphorous, carbon to nitrogen ratio, and heavy metals content) were analyzed. In addition, the seed germination, growth, and fresh head weight yield of each compost type were investigated on each matured compost type using cabbage seed (*Brassica oleracea)*. The results indicate that coffee husk and pulp can be composted alone or co-composted with SSMSW yielding very mature and stable compost with good quality, which is in the range of compost quality standards/guidelines set by different countries. It was confirmed that the addition of $1/4^{th}$ of local soil (wt/wt) on C8 compost type (the mixture of compost produced from $1/3^{rd}$ coffee pulp, $1/3^{rd}$ false banana leaves (*Ensete ventricosum*), and $1/3^{rd}$ soft dry woods), yields the optimum fresh head weight of the cabbage among all field trials. In addition, when C8 compost type is mixed with local soil in 3:1 ratio, it could yield an optimum fresh head weight of the cabbage (572 ± 10 g/kg of compost). This might be due to the relatively higher concentration of total nitrogen in the C8 compost sample. In general, the produced compost can be used for unrestricted agricultural purposes. Thus, co-composing of coffee husk and pulp with SSMSW can alleviate the multidimensional problems of rural and urban dwellers.

Keywords: Coffee husk, valorization, co-composting, maturity, compost quality, productivity

5.1 Introduction

In the previous chapters, particularly in chapter 3 and 4, the potential of different coffee waste fractions for bioethanol production and quality upgrading using pervaporation membranes was evaluated. In this chapter, the composting and co-composting potential of coffee husk and pulp by mixing it with source separated municipal solid waste in different ratio was evaluated. Coffee production and processing constitutes an important sector of the agro-industry in Ethiopia, accounting for up to 65% of the total exports from the country. In addition, approximately 15 million people (20% of the population) directly make a living from the coffee industry (Wiersum et al., 2008). Coffee processing industries are posing environmental hazards due to large-scale disposal of coffee pulp, husk and effluents into arable land and surface water (Preethu et al., 2007). The environmental impacts of coffee are enormous, with large quantities of solid and liquid waste generated globally (Hue et al., 2006). Over 10 million tonnes of solid residues are generated yearly from the coffee agro-industry worldwide, along with large amount of wastewater and cultivation residues (Echeverria and Nuti, 2017).

Even though coffee husk and pulp are rich in organic matter and nutrients, they also contain compounds such as caffeine, tannins, and polyphenols (Franca et al., 2009). Due to the presence of the latter compounds, the organic solid residues are toxic in nature, which not only adds to the problem of environmental pollution, but also restricts its use as animal feed (Pandey et al., 2000b). In this regard, the studies of Franca et al. (2009) indicated that coffee husk comprised of dry outer skin, pulp and parchment is probably the major residue from the handling and processing of coffee, since, for every kg of coffee beans produced, approximately 1 kg of husk is generated during dry processing. Similarly, Zoca et al. (2014) reported that since 50% of the harvested coffee is husk, it is important to consider that these byproducts can contribute to environmental problems if not disposed of properly. Thus, there is a need to find alternative uses for these residues.

In a life cycle analysis of coffee, Salomone (2003) reported cultivation and consumption of coffee as the two largest contributors of negative environmental impacts. In addition, Preethu et al. (2007) indicated that the presence of phytotoxic substances and organic acids in

coffee byproducts is affecting the soil, water quality and restricts the crop growth. However, coffee waste contains a high concentration of biodegradable organic compounds and minerals of plant origin, which can be utilized by composting with other organic materials.

Getahun et al. (2012a) reported that in Jimma town, Ethiopia, a considerable amount of waste ends up in open dumps without any sorting or treatment and is exposed to human and animal scavengers. Lemma and Tekilu (2014) reported that organic matter constitutes 92.5% of the municipal solid waste generated in Hosanna, Ethiopia, out of which 'chat' stalk constitutes 3%, which causes a major problem in logging the drainage and tipping additional pollution. The harvested green khat plant (received moist) is traditionally packaged as bundles of young shoots that are wrapped in the leaf of the false-banana plant to help maintain product freshness (Geisshüsler and Brenneisen, 1987). In Ethiopia, almost 10 million people are dependent on Ensete (*Ensete ventricosum)* also known as the false banana for different purposes (Pijls et al., 1995). The use of the leaves of false banana to retain khat's moistness and freshness for long-term storage is common in Ethiopia, where khat chewing is commonly practiced. However, it is afterward disposed into the local environment. Thus, sustainable solutions must be sought for its better management.

The use of organic compost in agriculture is a practice that brings many advantages, avoiding environmental contamination and nutrients immobilization, and is a source of organic matter in the soil (De Rezende et al., 2012). The treatment of coffee by-products through oxygen-driven biological methods such as composting would serve a dual purpose, i.e., fertilizer production and environmental protection (Murthy and Naidu, 2012). In this regard, Preethu et al. (2007) reported that treatment of coffee waste by composting reduces the severe damage that the application of immature compost to the soil would cause and allows a complete conservation of the residual energy stored in the organic material. Composting is a spontaneous biological decomposition process of organic materials in a predominantly aerobic environment (Bernal et al., 2009).

Composting is an oxidative decomposition process of organic matter assisted by microbial consortia under controlled conditions, producing a stabilized and sanitized end product (the compost), which is ready to be used as a fertilizer and soil conditioner (Cabañas-

Vargas et al., 2013). However, the detailed review conducted by Bernal et al. (2009) reported that while composting occurs naturally, efficient composting requires the control of several factors (bulk density, porosity, particle size, nutrient content, C/N ratio, temperature, pH, moisture and oxygen supply) to avoid nuisance problems such as odor, dust, and also for obtaining an agricultural product with high quality. In this regard, Yusuf (2008) indicated that composts can vary because of the raw materials used, the degree of decomposition, moisture content, nutrient content, salt content, acidity/ alkalinity and contaminants (organic and non-organic materials or heavy metals). A lower availability of nutrients may indicate incomplete decomposition or a low concentration of nutrients in the original material.

If compost is to be applied to land, its maturity and stability has to be assessed first. Otherwise, it may adversely affect the growth of plants due to the possible presence of pathogenic microorganisms and nutrients, which may disturb the nutrient balance of the soil where it is applied (Gazi et al., 2007). Getahun et al. (2012b) indicated that safe use of compost in agriculture depends on the production of good quality compost, specifically, compost that is mature and sufficiently low in metals and salt content (Getahun et al., 2012b). The detailed review conducted by Bernal et al. (2009) also indicated that the principal requirement of compost to be safely used in soil is a high degree of stability or maturity, which implies a stable organic matter content and the absence of phytotoxic compounds and plant or animal pathogens. The same study also indicated that when applying solid waste for composting, the heavy metal concentration in the compost and reference plant growth should be assessed.

Therefore, in this chapter, the composting and co-composting potential of coffee husk and pulp with source separated municipal solid waste is described in detail to answer the research gap, which is indicated in section 1.6 of the introductory chapter.

5.2 Methods and Materials

5.2.1 Coffee waste collection

Coffee husk and pulp were collected from dry and wet coffee processing plants, respectively in Yebbu town, Kersa district, Jimma zone, Ethiopia. The composting study was conducted at the Abdi Jimma community based waste management and composting micro-enterprise, Jimma town, Ethiopia. The municipal solid waste was collected from residential houses of Jimma town. The soft dry wood was collected from wood microenterprises found in Jimma town. Soft dry wood was used as a bulking agent to increase particle size and maintain an adequate porosity and aerobic conditions in compost piles. The collected coffee husk and pulp were stored in a dry place until composting has started. The municipal solid waste was sorted out and chopped. The biochar samples, which were prepared from the different coffee waste fractions, and, which were used for the germination, growth and yield productivity test of matured compost samples were obtained from the Department of Applied and Analytical Chemistry of Hasselt University, Belgium.

5.2.2 Experimental setup of the composting process

Twenty four piles were composted following the aerobic windrow composting method, subjected to manual turning. The compost had a volume of 1 m^3. The composting activity was conducted in triplicates and has the volume ratios as indicated in Table 5.1.

Table 5.1: Composition of composting piles and their category

Compost pile number	**Composition**	**Compost ID**
1-3	Coffee husk	C1
4-6	½ coffee husk and ½ SSMSW which is composed of fruits, vegetables and Khat *(Catha edulis*)	C2

7-9	SSMSW composed of fruits, vegetables and Khat/*Catha edulis*)	C3
10-12	1/3 coffee husk, 1/3 SSMSW composed of fruits, vegetables and Khat, and 1/3 soft dry wood	C4
13-15	Coffee pulp	C5
16-18	½ coffee pulp and ½ leaves of false banana (*Ensete ventricosum*), which is commonly known by the name of Ethiopian banana	C6
19-21	Leaves of false banana	C7
22-24	1/3 coffee pulp, 1/3 leaves of false banana, and 1/3 soft dry wood	C8

The composting activity was conducted for 3 months. The composting was undertaken in an open house with cemented floor and under a shade. The compost heaps/piles were covered with perforated HDPE plastic to prevent heat loss and to prevent the compost from drying. While turning the compost, the piles were watered after checking the moisture content of the samples. To optimize the composting parameters, the moisture content of the feedstock was adjusted to 50–60 % by sprinkling water on the surface of the composting mixture as suggested by Tiquia et al. (1998). Gajalakshmi and Abbasi (2008) also indicated that the optimum water content for composting varies with the waste to be composted, but generally the mixture should be at 50-60 %. The compost was turned 2-3 times a week during the first two active months of composting while the frequency of turning was reduced to only once a week afterwards.

5.2.3 Determination of physicochemical parameters

The samples from each experimental composting pile were collected weekly to monitor the changes in physico-chemical parameters (pH, electrical conductivity, organic carbon, available phosphorous and total nitrogen). All the samples were analyzed in triplicate and the mean results were reported. However, the temperature of the piles was recorded on a

daily basis for 90 days (12 weeks) and the weekly average result was reported. The compost samples were taken from each pile from all sides of the pile and thoroughly mixed to obtain a homogeneous and representative sample of the entire pile. Afterwards, it was ground using a pestle and mortar to pass through a sieve to minimize sub-sample variability (Dadi et al., 2012). The temperature was measured using a glass thermometer onsite. The pH and EC were measured using a Hach multi-meter probe (P/N HQ40d multimeter). The concentration of organic carbon, available phosphorus, and total nitrogen were determined using the Van Reeuwijk (1993), Olsen (1954) and Kjeldahl (Bremner, 1960) methods, respectively. The physicochemical parameters (temperature, pH, EC, organic carbon, total nitrogen, C/N ration, and available phosphorous) data were analyzed with Statistical Analysis System (v. 9.2, SAS Institute Inc., Cary, NC USA,) software. Furthermore, the mean significant difference between the compost types was declared using LSD (P=0.05). The concentration of potassium and heavy metals (Cd, Cr, Cu, Ni, Pb, Zn, Fe and Mn) of the composted samples were analyzed only for matured and stable compost.

5.2.4 Methods of digestion for heavy metal concentration analysis

The potassium and heavy metal concentration of the matured and stable compost samples were analyzed at the Environmental Public Health Laboratory of Ethiopian Public Health Institute, Addis Ababa, Ethiopia using Atomic Absorption Spectrometry (AAS). Before analyzing the heavy metals, each compost sample was dried at 65 °C for 48 h and then digested using the nitric acid digestion method. One gram of sample was placed in a 250 ml digestion tube and 10 ml of concentrated HNO_3 was added. The sample was heated for 45 min at 90 °C, and then the temperature was increased to 150 °C at which the sample was boiled for at least 8 h until a clear solution was obtained. Concentrated HNO_3 was added to the sample (5 ml was added at least three times) and digestion occurred until the volume was reduced to about 1 ml. The interior walls of the tube were washed down with distilled water and the tube was swirled throughout the digestion to keep the wall clean and prevent the loss of the sample. After cooling, 5 ml of 1% HNO_3 was added to the sample. The solution was filtered with Whatman No. 42 filter paper and < 0.45 µm Millipore filter paper. It was then

transferred quantitatively to a 25 ml volumetric flask by adding distilled water. This approach was adopted from Hseu (2004).

5.2.5 Germination and vegetable productivity test of the matured compost samples

Before sowing the seed of cabbage on the composted samples, equal proportions of compost samples (1 kg each) was filled in plastic bags and watered with tap water to make the compost samples wet for a few days. Afterwards, each seed of the cabbage was sown on the compost samples. To check the maturity of the produced compost samples, the vegetable cabbage (*Brassica oleracea)* seed was sown on the 1 kg of composted samples using the local soil as a control. Biochar is used to assess whether the fresh head weight of the cabbage (productivity) is increased or not by using biochar. Thus, 10 g of the biochar sample that was prepared from the mix of different coffee waste samples (husk, parchment, silver skin, spent coffee and pulp) at equal proportions was used for germination, growth and productivity tests. Thus, the ratio of biochar sample to soil/composted sample is only 1% (wt/wt). Cabbage (*Brassica oleracea)* was chosen for the study since it is a commonly grown vegetable in the study area. The germination study was conducted in the shade to prevent excess water loss and wilting of the seedlings. Afterwards, the germinated seedlings were transplanted to the local soil with their plastics cover. Each seedling was monitored carefully and the final fresh head weight of the cabbage was noted.

5.3 Results and discussion

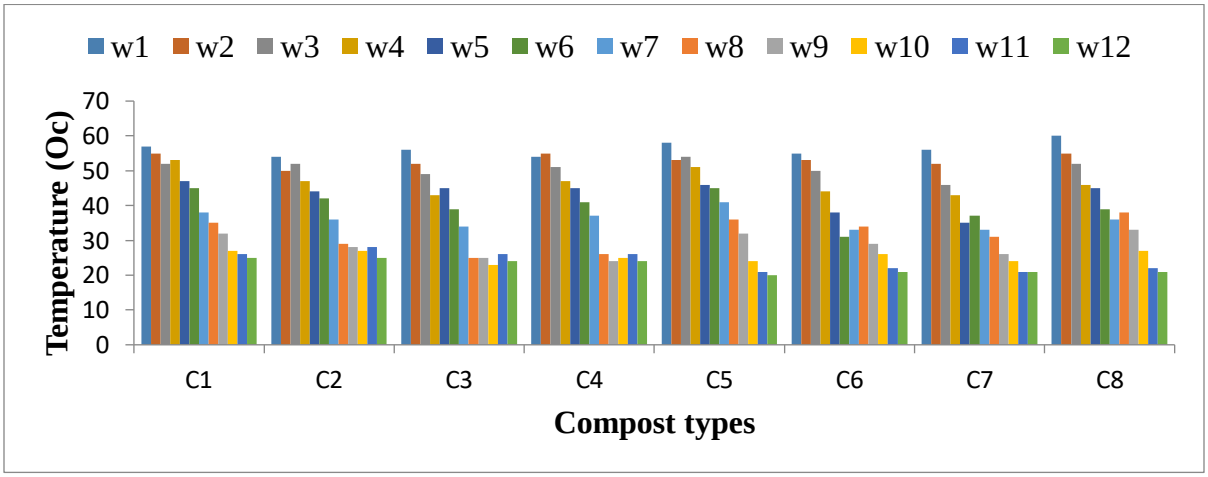
The results of the weekly average temperature of the composting piles are shown in Figure 5.1.

5.3.1 Temperature (^{o}C)

As shown in Figure 5.1, C1 and C5 compost types have a higher mesophilic temperature range until the 10^{th} week of composting, and C6 and C7 compost types have a lower

mesophilic temperature than the other compost types. The sharp decrement of temperature in C6 and C7 compost types during the composting process could be a result of a lower level of microbial activity due to a lower availability of easily degradable organic materials. This might be due to the fact that during the composting process, microorganisms degrade the organic matter in the waste with the production of heat, NH_3, CO_2, organic acids and water vapor (Bernal et al., 2009). The heat released is trapped within the pile leading to the phenomenon of self-heating, which is responsible for the rise in the temperature of the pile at the initial phase of composting (Ryckeboer et al., 2003).

Types of compost showed a highly significant effect on the mean temperature ($P < 0.0001$). Highly significant differences in mean temperature were recorded between the compost types C1 and C4; C1 and C6; C1 and C7; C2 and C7; C3 and C5; C5 and C6; C5 and C7; C6 and C8; C7 and C8 with the p-value 0.0002, 0.0055, 0.0001, 0.0001, 0.0055, 0.0028, 0.0009, 0.0001, 0.0044 and 0.0003, respectively ($LSD_{0.05}$ =1.0804). These differences in temperature might be due to the differences in the nutrient content (carbohydrates, fats, aminoacids, cellulose, hemicelluloses, and lignin) of the source materials, the presence/absence of volatile/nonvolatile compounds, moisture content, the mixing ratio, particle size of the feedstock, aeration, mechanical structure, porosity, the availability and abundance of microorganisms as well as the interaction within the composted materials during composting.



***** W = Week; C = Compost type

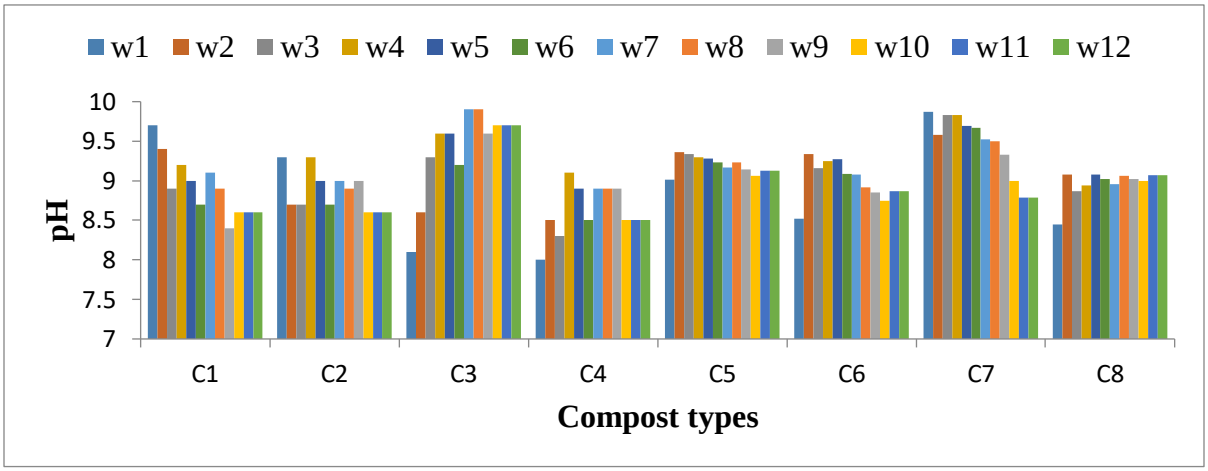
Fig. 5.1 Temperature of composting piles as a function of the duration of composting

In well-controlled composting, the temperature increases rapidly in the initial phase, reaches a maximum in the active phase and then comes back to ambient temperature in the cooling phase (Hassen et al., 2001). The regulation of the temperature is required for controlled composting. In this regard, the study of Miller (1993) indicated that the range of 52-60 ^{o}C is the most favorable for decomposition. In general, as composting proceeds, the temperature of all of the compost types declines, which is in agreement with previous studies (Dadi et al., 2012). At the beginning of the composting process, all the piles were in a thermophilic stage since the temperature exceeded 55 ^{o}C. However, the temperature started to drop to 25 ^{o}C and below during the final stage of composting. The slight increases in the pile temperatures immediately after each turning operation in the early days of composting are attributed to the re-activation of the composting process, which is explained by mixing to provide a degradable substrate from the surface or external parts of the composting pile for the microbial biomass in the center (Getahun et al., 2012b).

5.3.2 pH

As shown in Figure 5.2, the pH of all of the compost piles varied within weeks in an irregular way. However, starting from the 10th week of composting period, the pH value was stabilized due to the buffering nature of humic substances (Preethu et al., 2007). For compost types C1, C2 and C7, in general, the pH was found to decrease starting from the first week of composting, while for the others, the pH was found to increase. The decrease in pH of decomposing organic materials might be due to the production of organic acids, phenolic compounds and the further increase in pH might be due to the formation of ammonia during decomposition (Preethu et al., 2007). The study of Liu and Price (2011) indicated that the decrement of the pH could be the result of the carbon dioxide evolution in the composting pile, and the accumulation of organic acids during the composting process. A pH decrease from about 8.3 at the initial stage of composting to 7.7 in the final phase of composting was also reported by Getahun et al. (2012b). The relatively low pH of C4 may be due to the presence of acids in these materials, which is in agreement with the study of Preethu et al. (2007).

Types of compost showed a highly significant effect on mean pH (P<0.0001). Highly significant differences in mean pH were recorded between the compost types C1 and C3; C1 and C7; C2 and C3; C2 and C7; C3 and C4; C3 and C6; C3 and C8; C4 and C5; C4 and C6; C4 and C7; C4 and C8; C6 and C7; and C7 and C8 with the p-value 0.0003, 0.0001, 0.0001, 0.0001, 0.0001, 0.0020, 0.0010, 0.0001,0.0048, 0.0001, 0.0091, 0.0007, and 0.0003, respectively ($LSD_{0.05}$ = 0.1282). The difference in pH among the composted types might be due to the differences in the presence/absence of volatile/nonvolatile substances in the feedstock, chemical composition of the starting materials, the mixing ratio and the interaction within the composted materials during composting.



***** W = Week; C = Compost type

Fig. 5.2 pH of composting piles as a function of the duration of composting

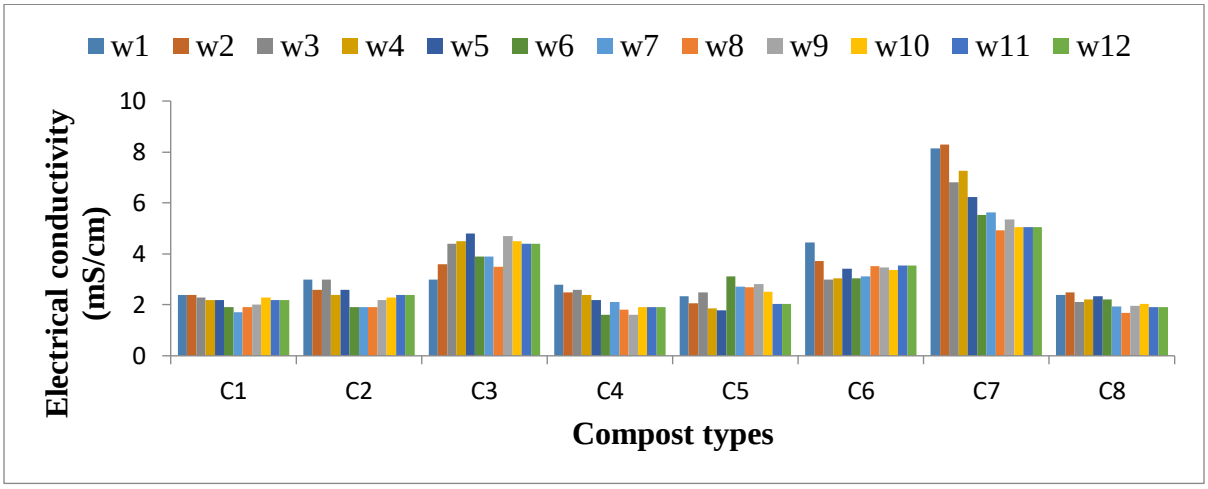
The increase in pH during initial composting phase is probably the result of ammonia release from ammonification (Bustamante et al., 2008). The presence of volatile fatty acids may also influence the pH development in the compost piles (Beck et al., 2001; Yusuf, 2008). When the pH of the soil is above 7.2, the ammonium ion will be converted to ammonium gas which can be lost to the atmosphere (Tack, 2013). In general, the combined effects of ammonification and accumulation of organic acids regulate the pH dynamics

during the composting process (Liu and Price, 2011). Finally, for all compost types, the pH of matured compost samples was measured to be slightly basic (8.5 ± 0.0 - 9.7 ± 0.0). This implies that the matured compost samples of this study are promising and can be used as the treatment of acidic soils since they do not need the addition of chemicals to balance the pH before applying it to soils.

5.3.3 Electrical Conductivity (EC)

The EC value indicates the concentration of ions available in the compost. Figure 5.3 suggests that in general, the EC of all compost types (except C3) declines with time. This might be due to ammonia volatilization and precipitation of mineral salts (Kassegn et al., 2015). Additionally, the decreasing pattern in EC during composting might be due to leaching of salts from the composting piles resulting from watering. The same observations were reported by Getahun et al. (2012b). On the contrary, even though there are irregularities, the EC of C3 compost type was found to increase with time. Similar observations were reported in the literature (Shemekite et al., 2014). The increase in EC might be due to the slight increase in potassium ions (K^+) and other ions as decomposition proceeds. In addition, it could be due to the release of mineral salts such as phosphates and ammonium ions through the decomposition (Bernal et al., 2009; Liu and Price, 2011; Dadi et al., 2012).

Types of compost showed a highly significant effect on mean EC (P<0.0001). Highly significant differences in mean EC were recorded between the compost types C1 and C3; C1 and C6; C1 and C7; C2 and C3; C2 and C6; C2 and C7; C3 and C4; C3 and C5; C3 and C6; C3 and C7; C3 and C8; C4 and C6; C4 and C7; C5 and C6; C5 and C7; C6 and C7; C6 and C8; and C7 and C8 all with the p-value 0.0001 ($LSD_{0.05}$ = 0.2191). These differences in EC among the composted types might be due to the differences in the moisture content, chemical composition of the starting substances, leaching/precipitation of nutrients, the mixing ratio and the interaction within the composted materials during composting.



***** W = Week; C = Compost type

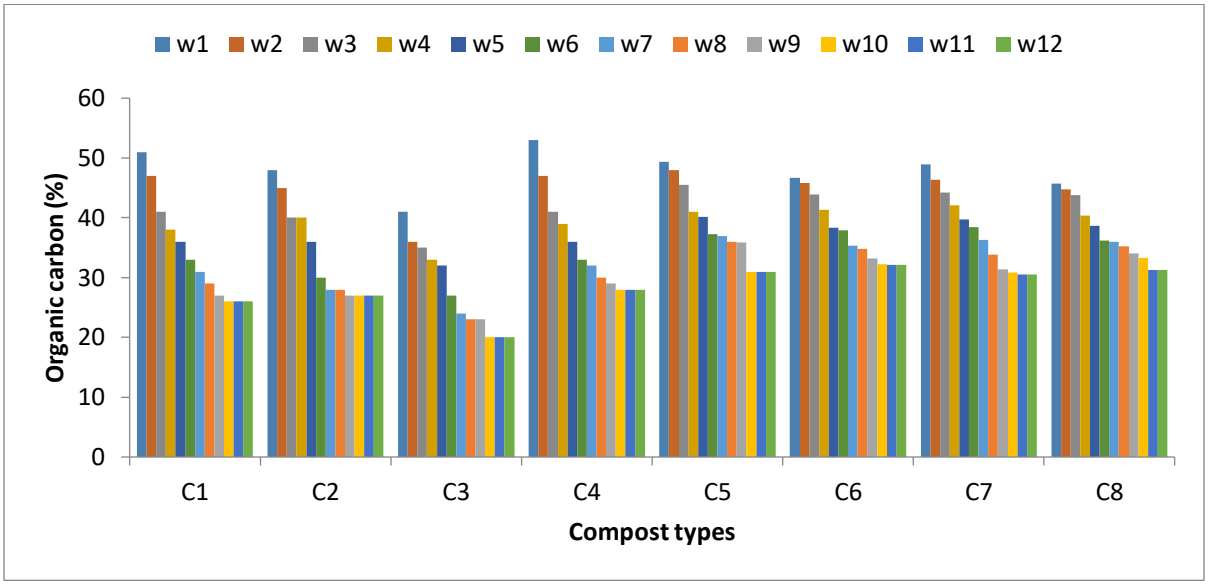
Fig. 5.3 Electrical conductivity of composting piles as a function of the duration of composting

In general, the EC is higher in the final product than in the initial mixture due to the release of soluble salts (Huang et al., 2004; Wang et al., 2004), but the EC may decrease due to the volatilization of ammonia and the precipitation and leaching of mineral salts. In general, the EC values of matured compost types were in the common range for most composts and in agreement with the study of Yusuf (2008), which reported the EC values of matured compost samples in the range of 2.19 to 9.32 mS/cm**.** Overall, the EC values indicate that application of these matured compost types for agricultural purposes will not damage the crops/vegetables, as indicated by Mamo (1998), who reported that most plants could not tolerate a soluble salt content above 4000 mS/cm. From the results shown in Figure 5.3, it can be observed that the EC value of compost produced from C3 and C7, which is composed of SSMSW (fruits, vegetables, Khat/*Catha edulis* and false banana leaves) is higher when composted alone than co-composting it with coffee waste. This might be a reason for the observation of highly significant differences for both C3 and C7 compost types with all the remaining compost types.

5.3.4 Organic Carbon (OC) (%)

As shown in Figure 5.4, the organic carbon content of all of the compost types declines with time. During the active phase of the composting process, the organic matter content decreases in the material due to decomposition of the organic matter by the microorganisms. This loss of organic matter reduces the weight of the pile and decreases the C/N ratio. The degradation rate of the organic matter/carbon decreases gradually as composting progress because of the reduction in available carbon sources, and synthesis reactions of the new complex and polymerized organic compounds (humification) prevail over mineralization during the maturation phase (Bernal et al., 2009). This process leads to stabilized end-products, which act as slow-release fertilizers for agricultural purposes. Kassegn et al. (2015) also indicated that the organic carbon content of compost samples has a consistently decreasing tendency over the composting time, and reported a % OC of 55.12 at the beginning and 15.69 at the end. This might be due to the loss of carbon as CO_2 during composting, as indicated by Getahun et al. (2012b), who found a loss of carbon from about 44 % at the beginning to 17 % during the maturing phase.

The type of compost showed a highly significant effect on the mean OC ($P < 0.0001$). Highly significant differences in mean OC were recorded between all the compost types except no significant differences were observed between C1 and C2; C1 and C4; C5 and C6; C5 and C7; C5 and C8; C6 and C7; C6 and C8; and C7 and C8 with the p-value 0.3598, 0.1385, 0.2927, 0.2531, 0.1541, 0.9268, 0.7050, and 0.7742, respectively ($LSD_{0.05} = 0.7237$). These differences in OC among the composted types might be due to the differences in the organic/inorganic content as well as the presence/absence of volatile compounds (biochemical composition) of the starting substances, aeration, the mixing ratio and the interaction within the composted materials during composting.



* W = Week; C = Compost type

Fig. 5.4 Organic carbon of composting piles as a function of the duration of composting

The findings in the present study are consistent for values reported in other conditions (Preethu et al., 2007; Liu and Price, 2011; Shemekite et al., 2014). It was observed that comparable amounts of organic carbon were obtained for compost types C1, C2 and C4 during the maturing stage of the composting process. Similarly, C5, C7 and C8 compost types were observed having a comparable amount of OC at the maturity phase of composting. However, the organic carbon content of C3 sample was lower than for all the other compost types in almost all stages of the composting process. This might be because of the absence of coffee husk and pulp in the mixture, which has a high lignocellulosic content. Besides, the relatively higher OC content of C6 compost type may be from the chemical interaction that takes place from the equal mix of coffee pulp and leaves of false banana.

Generally, the organic carbon values were found to decrease from the initial composting period to the final composting stage. It has indeed been found that the volume of all composting piles was reduced significantly. The volume reduction is attributed to the decomposition of organic substances and compaction (Yusuf, 2008). These results are in agreement with the study of Anandavalli et al. (1998), which confirmed the reduction of organic carbon with time.

5.3.5 Total Nitrogen (TN) (%)

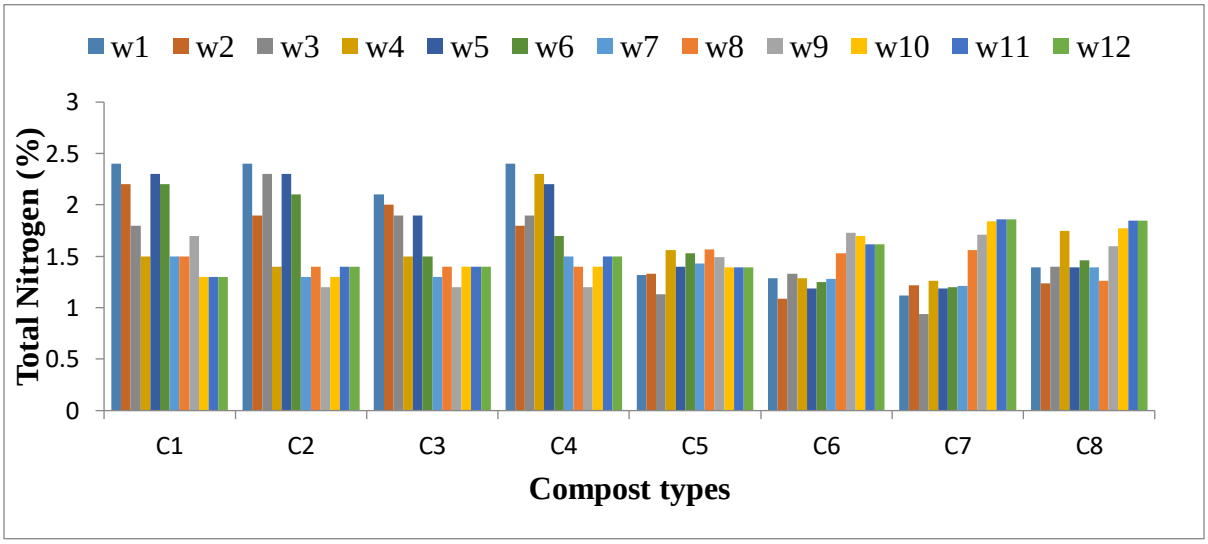
Typically, the soil organic matter contains about 5% nitrogen (Tack, 2013). The main forms of nitrogen that can be taken up by plants is as either ammonium or nitrate. Figure 5.5 shows that for C1-C4 composting types the total nitrogen content declines with time. This might be due to turning, which exposes the fresh material to microbial colonization and leads to the release of NH_3 that has accumulated in the internal void spaces of the compost (Ogunwande et al., 2008; Tirado, 2008; Kalamdhad and Kazmi, 2009; Getahun et al., 2012b). Kassegn et al. (2015) found that the total nitrogen content of compost samples showed a consistently decreasing tendency over the composting time (1.32 % TN initially and 1.03 at the end). This decrease of carbon and nitrogen contents in the compost is likely due to their consumption by microorganisms for their proper functioning. Carbon is used as energy source and nitrogen for protein synthesis by bacteria, which leads to their rapid proliferation during the initial stage of composting (Adegunloye et al., 2007; Varma and Kalamdhad, 2013).

At the maturity phase, the TN content of all the composting types was found to be in the range 1.30 ± 0.10 - 1.86 ± 0.28 %. Since the matured compost samples have a TN over 1%, they have fertilizing capability and can be used in agriculture and hence no supplemental N is needed. These results are in agreement with the study of Yusuf (2008), which reported the TN content of matured compost samples in the range of 0.9 to 1.40 %. Similar observations were reported by Dadi et al. (2012). The irregularities in total nitrogen amount of each of the composting types within weeks may be due to variation in decomposition rate of organic matter in the mixture. In support of this, the study of Sánchez-Monedero et al. (2001) indicated that the concentration of the different forms of N and their evolution during composting depends on the original material (feed stock) that provides the N to the mixture in the first place and on its organic matter degradation rate.

Contrary to the trend of C1-C4 composting types, the total nitrogen content for all the remaining composting types (C5-C8) was observed to increase with time. These results are in agreement with some other studies (Preethu et al., 2007; Liu and Price, 2011; Shemekite et

al., 2014), which reported a slight increment in the TN content from the composting of coffee waste as decomposition proceeded. These differences might be due to the difference in the composition and type of composted materials. In support of this, the study of Sánchez-Monedero et al. (2001) confirmed that nitrogen losses during composting depend on the materials used and on the pH of the mixtures. The study of Yusuf (2008) also indicated that composts can vary because of the raw materials used, degree of decomposition, moisture content, nutrient content, salt content, acidity/ alkalinity and contaminants (organic and non-organic materials or heavy metals).

In general, as shown in Figure 5.5, the TN content of all of the compost piles varied within weeks in an irregular way. Besides, C6, C7, and C8 compost types were measured to have a higher TN content than all the remaining composting systems at the maturity stage. This might be from the leaves of false banana, which is a common constituent of the three composting piles.



***** W = Week; C = Compost type

Fig. 5.5 Total nitrogen of composting piles as a function of the duration of composting

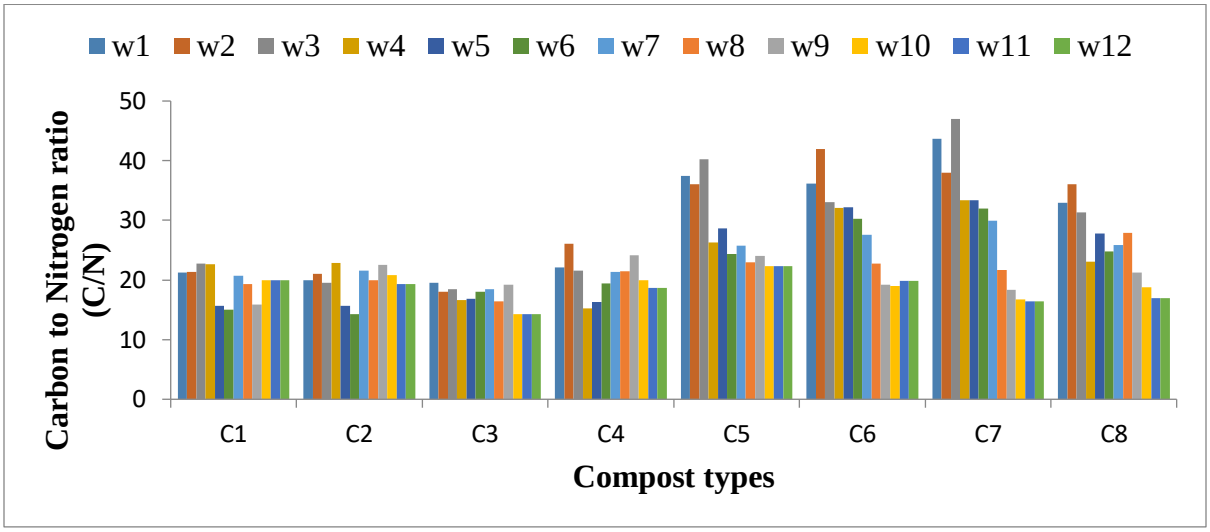
Types of compost showed a significant effect on mean TN (P=0.0243). A significant differences in mean TN were recorded between the compost types of C1 and C5; C1 and C6;

C1 and C7; C2 and C5; C2 and C6; C2 and C7; C4 and C5; C4 and C6; and C4 and C7 with the p-values 0.0128, 0.0126, 0.0136, 0.0328, 0.0323, 0.0348, 0.0177, 0.0174, 0.0188, respectively ($LSD_{0.05}$ = 0.1330). A possible explanation for the differences in TN among the composted types might be due to the differences in the mineralization/immobilization of nitrogen at different stages of composting, chemical composition (such as fats, aminoacids, nitrogen content and forms of nitrogen) of the starting substances, the mixing ratio and the interaction within the composted materials during composting as explained in sub-sections 5.3.1-5.3.4.

5.3.6 Carbon to Nitrogen (C/N) ratio

The C/N ratio is one of the major factors affecting the quality of compost. The results in figure 5.4 and 5.5 indicated that as the duration of composting increases, from the first week to the 12th week, the organic carbon fraction declines, whereas the total nitrogen concentration varies with time. This implies that the C/N ratio of all composting types varies with time. However, in general, the C/N ratio of all composting types was observed to decline with time, which indicates that a stable product is formed. This is indicated in Figure 5.6. Previous studies (Liu and Price, 2011; Dadi et al., 2012; Getahun et al., 2012b; Shemekite et al., 2014) also reported a decrement of C/N values with time. Types of compost showed a highly significant effect on mean C/N (P<0.0001).

Highly significant differences in mean C/N were recorded between all the compost types except no significant differences were observed between C1 and C2; C1 and C3; C1 and C4; C2 and C3; C2 and C4; C3 and C4; C5 and C6; C5 and C7; C5 and C8; C6 and C7; C6 and C8; C7 and C8 with the p-values 0.9222, 0.1824, 0.6431, 0.1529, 0.7145, 0.0741, 0.9582, 0.5239, 0.1987, 0.5585, 0.1813, and 0.0564, respectively ($LSD_{0.05}$ = 1.8704). A possible explanation for the differences in C/N among the composted types might be due to the differences in the organic carbon content, the mineralization/immobilization of nitrogen at different stages of composting, chemical composition of the starting feedstock, and the role of microorganisms during composting as indicated in sub-sections 5.3.1-5.3.5.



***** W = Week; C = Compost type

Fig. 5.6 C/N ratio of composting piles as a function of the duration of composting

During the maturing phase of the composting process, the C/N ratio of C3 and C7 compost was found to be the lowest of all compost types. The reason is that C3 and C7 compost types had the lowest organic carbon and the highest TN content, respectively, among all compost types (see Figures 5.4 and 5.5). In general, during the maturing phase, the compost types C5 and C1 were found to have higher C/N values than the others. This might be due to the composition of coffee byproducts (coffee husk and pulp) used for composting. In this regard, the findings of Shemekite et al. (2014) clearly confirmed that higher C/N ratios were obtained when coffee husk is composted alone than by co-composting it with either cow dung or fruit/vegetable waste.

A higher C/N ratio at the end of the composting process for the coffee pulp and coffee husk compost (C5 and C1, respectively) was found, indicating a slow kinetic process in this compost. The study of Shemekite et al. (2014) confirmed that the addition of cow dung and fruit/vegetable waste to coffee husk significantly contributed to the decomposition of the lignocellulosic compounds of the husk, resulting in higher N losses in these mixed composts. Furthermore, the study of Sánchez-Monedero et al. (2001) also reported that the use of waste

fractions with a high lignocellulosic content in the mixtures led to lower N losses during the composting process than observed in the mixture of MSW, which lost more of its N content.

Although there is no universally accepted method of evaluating compost maturity and stability, one of the most commonly used methods of checking is the carbon to nitrogen ratio (CCQC, 2001). The C/N ratio of the matured compost samples is in agreement with the suggestions of Liu and Price (2011), which indicated that a final compost is considered stable and hence mature if it has a C:N ratio of < 25:1. Furthermore, the results are within the range recommended by the Ethiopian Environmental Protection Authority (EEPA) good quality compost guidelines, which recommend a C/N ratio of 29:1 or less (EFEPA, 2004). Thus, the C/N for the final compost sample obtained in this study, which is in the range of 14.29 ± 1.68 - 22.28 ± 2.56, lies reasonably within the acceptable range for use in agriculture. Thus, all the produced compost samples (C1-C8) can be used for agricultural purposes.

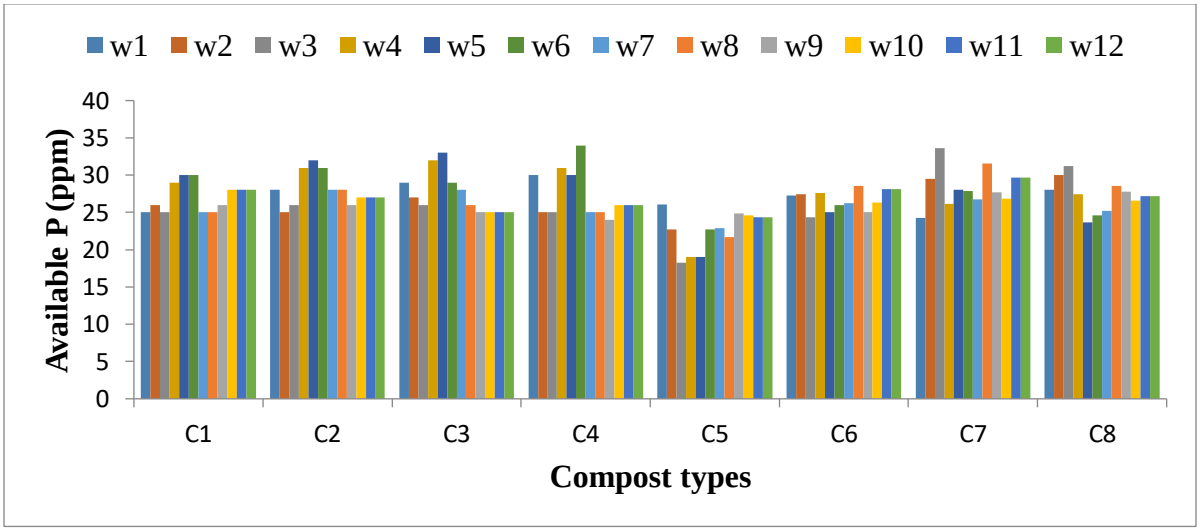
5.3.7 Available Phosphorous

Phosphorus in soils occurs exclusively as orthophosphate. Generally, organic phosphorus varies along with the organic matter content and therefore tends to be higher in topsoils and lower in subsoils. Most of the phosphorus in soils is largely unavailable to plants. Orthophosphate is the most stable form of phosphate in soils. The dominant orthophosphate form in solution will, therefore, depend on pH. The concentration of P in the soil solution is normally between 0.3 and 3 mg/L. Phosphate is most available to plants at neutral pH. Phosphates are immobilized at acidic pH as iron and aluminum phosphates, and at alkaline pH as calcium phosphates (Tack, 2013).

As shown in Figure 5.7, the available phosphorous content of all of the compost piles varied within weeks in an irregular way. The increment of available phosphorous within the composting weeks may be from the release of inorganic phosphate from organic phosphates (mineralization**),** which is caused by microorganisms breaking down organic compounds. On the other side, the decrement of available phosphorous could be due to its leaching or precipitation by forming insoluble phosphates by reactions with positively charged cations of

metals in the compost (Varma and Kalamdhad, 2013). The study of Kassegn et al. (2015) on MSW compost samples reported a decrement of available phosphorus with composting time.

Types of compost showed a highly significant effect on mean AP (P<0.0001). Highly significant difference in mean AP was recorded between C5 compost type with all the rest ($LSD_{0.05}$ = 0.9928). A possible explanation for the differences in available phosphorus among the composted types might be due to the nutrient content of the starting substances (such as simple carbohydrates, fats, amino acids, cellulose, hemicelluloses, and lignin), the mixing ratio, the available microorganisms, stability, maturity, and the interaction within the composted materials during composting.



* W = Week; C = Compost type

Fig. 5.7 Available phosphorous of composting piles as a function of the duration of composting

In general, the available phosphorous content for the final compost sample obtained in this study is in the range of 24.32 ± 1.06 – 29.69 ± 1.06 ppm. In this regard, Getahun et al. (2012b) reported the total phosphorous content of matured compost samples ranging from 1.61 to 2.24 g/kg. Yusuf (2008) reported the available phosphorus content of matured compost ranging from 532.00 to 803.00 ppm from Khat and related materials composting.

These differences in available phosphorous content might be due to the differences in raw materials used for composting, composting system and composting time. C5 and C7 composts were measured to have the lowest and highest content of available phosphorous, respectively, among all compost types.

5.3.8 Available potassium

Potassium exists in the soil as dissolved K^+ ions (solution K), exchangeable K, nonexchangeable K, and mineral K. Plants can only directly absorb solution K, yet solution K concentrations range from only 1 to 10 mg/L. Plant available K includes solution K and exchangeable K. The processes governing the availability of K are mineral weathering, clay fixation and release, sorption and desorption, leaching, erosion, and plant uptake. K has been traditionally expressed as potash, or K_2O, although K does not actually exist in this form in the soil (Tack, 2013).

The concentration of available potassium in matured and stable compost samples C1, C2, C3, C4, C5, C6, C7 and C8 were measured to be 466.50 ± 88.77, 458.17 ± 103.24, 459.00 ± 68.05, 360.67 ± 36.43, 485 ± 44, 426 ± 36, 471 ± 43, and 403 ± 33 mg/kg, respectively. The highest concentration of potassium was detected in C5 and C7 composts, and the lowest concentration of potassium was detected in C4 and C8 compost samples among all compost samples. The relatively higher K content measured in the composts may be due to the higher concentration of K in the raw materials (i.e., in coffee pulp and the leaves of false banana, respectively). This is supported by the study of Preethu et al. (2007), which reported the compost sample of coffee husk and pulp containing 2.94 % K. Yusuf (2008) reported the available potassium content of matured compost sample of Khat and related materials to be in the range of 6775.72 to 12445.24 ppm. Getahun et al. (2012b) reported a potassium content of matured compost samples ranging from 0.69 to 1.15 g/kg.

5.3.9 Heavy metals concentration of matured compost samples

The heavy metal (Pb, Cr, Cd, Mn, Zn, Fe, Ni, and Cu) content of the matured compost samples were analyzed and the results are shown in Table 5.2.

Table 5.2: Heavy metal content of the matured compost samples (all units in mg/kg)

Compost type	Cd	Co	Hg	Fe	Mn	Ni	Zn	Cu	Cr	Pb
C1	0.45 ± 0.33			173.67 ± 54.83	2.34 ± 0.46	0.55 ± 0.16	2.40 ± 0.51	0.02 ± 0.00	nd	nd
C2	1.19 ± 0.43			1092.91 ± 261.06	6.46 ± 2.96	0.59 ± 0.42	2.40 ± 1.19	0.02 ± 0.00	nd	nd
C3	2.23 ± 0.29			923.60 ± 386.92	9.79 ± 6.63	nd	3.48 ± 1.53	0.02 ± 0.00	nd	nd
C4	3.18 ± 0.32			266.85 ± 179.32	5.28 ± 1.67	nd	2.23 ± 0.32	0.02 ± 0.00	nd	nd
C5	nd			479 ± 221	3.28 ± 0.65	0.47 ± 0.06	0.62 ± 0.08	0.24 ± 0.02	nd	nd
C6	nd			466 ± 165	4.28 ± 0.64	0.59 ± 0.05	0.62 ± 0.07	0.18 ± 0.02	nd	nd
C7	nd			2033 ± 1005	9.13 ± 1.85	0.75 ± 0.05	0.98 ± 0.19	0.17 ± 0.03	nd	nd
C8	nd			897 ± 355	7.20 ± 1.13	0.82 ± 0.06	0.80 ± 0.14	0.22 ± 0.03	nd	nd
CCME (2005)*	3					62	700	400	210	150
Belgium (agricultural use)**	5	10	5			50	1000	100	150	600
EU Range**	0.7-10		0.7-10			20-200	210-4000	70-600	70-200	70-1000
USA** Biosolids	39		17			420	2800	1500	1200	300

ND = not detected

* Canadian Council of Ministers of the Environment (CCME, 2005), Guidelines for Compost Quality Maximum Concentration for unrestricted use

** Heavy metals limits (Brinton, 2000)

As shown in Table 5.2, the Pb and Cr concentration was below the detection limit of the instrument and were undetected in all compost samples. Ni was detected in all compost samples with the concentration of less than 1 ppm. However, it was not detected in C3 and C4 composts. This confirmed that coffee husk, pulp, and leaves of false banana contained Ni. Cu was detected uniformly in all the matured compost samples with a concentration below 0.30 mg/kg. Higher concentrations of Mn in C3 and C7, and Zn in C3 compost samples were detected than in other compost types. This might be related to the MSW source; for example, it can be from the raw material itself, electronic equipment, packaging materials, dry batteries, etc. C3 and C4 compost samples were found to have a higher amount of Cd than the other compost types. The main source of Cd in these compost samples may be from ointments, paints, inks, dry batteries, toys, electronic equipment, etc. in contact with MSW during collection. On the other hand, the highest concentration of iron was detected in C7 compost. Getahun et al. (2012b) reported iron content of matured compost samples ranging from 1.75 to 2.62 g/kg. A higher iron content of the sample of false banana was also reported by Abebe et al. (2007).

In general, the concentrations of all the analyzed metals in the matured compost samples are in the range of compost quality standards/guidelines set by Belgium (for agriculture), the European Union, the USA (for biosolids), and the Canadian Council of Ministers of the Environment (CCME, 2005) guidelines for compost quality for unrestricted use.

5.3.10 Germination test and yield of fresh head weight of cabbage

The results of the growth of cabbage seeds on the matured compost samples, its nature of germination, as well as the yield of the fresh head weight of the grown cabbage are

indicated in Table 5.3. For the germination study, the number of seeds that are germinating were counted and all seeds were found to germinate and grew on composted samples. This, in turn, implies that all the produced compost samples were rated very mature since all the sown cabbage seeds (*Brassica oleracea)* were germinating and grew.

Table 5.3: Germination, growth, and yield productivity test on composted samples

S.No	**Type of applied compost**	**Amount of local soil**	**Amount of biochar used (g)**	**Nature of germination**	**Head weight of the cabbage (g) per kg of compost (soil)**
1.	-	100 %	-	Very Slow	94 ± 8
2.	C1	-	-	Moderate	134 ± 4
3.	¾th C1	¼th soil	-	Moderate	146 ± 5
4.	½ C1	½ soil	-	moderate	160 ± 6
5.	¼th C1	¾th soil	-	Slow	116 ± 6
6.	½ C1	½ soil	10	Fast	172 ± 6
7.	C1	-	10	Moderate	146 ± 4
8.	-	Soil	10	Slow	108 ± 4
9.	C2	-	-	Moderate	221 ± 7
10.	¾th C2	¼th soil	-	Moderate	202 ± 8
11.	½ C2	½ soil	-	Moderate	191 ± 6
12.	¼th C2	¾th soil	-	Slow	178 ± 10
13.	½ C2	½ soil	10	Fast	204 ± 10
14.	C2	-	10	Moderate	217 ± 6

15.	C3	-	-	Moderate	171 ± 9
16.	¾th C3	¼th soil	-	Moderate	171 ± 8
17.	½ C3	½ soil	-	Moderate	155 ± 8
18.	¼th C3	¾th soil	-	Slow	155 ± 5
19.	½ C3	½ soil	10	Fast	163 ± 5
20.	C3	-	10	Moderate	178 ± 4
21.	C4	-	-	Fast	276 ± 6
22.	¾th C4	¼th soil	-	Fast	260 ± 7
23.	½ C4	½ soil	-	Fast	218 ± 5
24.	¼th C4	¾th soil	-	Moderate	173 ± 6
25.	½ C4	½ soil	10	Fast	226 ± 5
26.	C4	-	10	Fast	279 ± 7
27.	C5	-	-	Slow	107 ± 3
28.	3/4th C5	1/4th soil	-	Moderate	125 ± 13
29.	½ C5	½ soil	-	Moderate	133 ± 10
30.	1/4th C5	3/4th soil	-	Moderate	118 ± 8
31.	½ C5	½ soil	10	Fast	140 ± 5
32.	C5	-	10	Moderate	117 ± 8
33.	C6	-	-	Moderate	302 ± 10
34.	3/4th C6	1/4th soil	-	Moderate	287 ± 10
35.	½ C6	½ soil	-	Moderate	278 ± 8

36.	1/4th C6	3/4th soil	-	Slow	225 ± 5
37.	½ C6	½ soil	10	Fast	288 ± 10
38.	C6	-	10	Moderate	212 ± 8
39.	C7	-	-	Moderate	243 ± 10
40.	3/4th C7	1/4th soil	-	Moderate	252 ± 10
41.	½ C7	½ soil	-	Moderate	192 ± 10
42.	1/4th C7	3/4th soil	-	Slow	175 ± 10
43.	½ C7	½ soil	10	Fast	202 ± 10
44.	C7	-	10	Moderate	253 ± 10
45.	C8	-	-	Fast	533 ± 13
46.	3/4th C8	1/4th soil	-	Fast	572 ± 10
47.	½ C8	½ soil	-	Fast	482 ± 15
48.	1/4th C8	3/4th soil	-	Moderate	422 ± 8
49.	½ C8	½ soil	10	Fast	493 ± 10
50.	C8	-	10	Fast	545 ± 10

According to Zucconi et al. (1981), a germination index below 50 % characterizes an immature compost. According to TMECC (2002), a compost with a C/N > 25 is immature. Immature and poorly stabilized composts may pose a number of problems during storage, marketing and use (Bernal et al., 2009). Therefore, as indicated in Table 5.3, all the produced compost samples were rated very mature since all the sown cabbage seeds (*Brassica oleracea)* were germinating and grew. This implies that the produced compost samples are free of plant phytotoxic materials (Dadi et al., 2012). Furthermore, the seeds of cabbage were observed to grow very slowly either when either the local soil alone or ¾ of it and ¼th of

compost samples of all types (C1-C8) were used. In addition, the fresh head weight of the cabbage yield obtained was also very low. This might be due to lack of nutrients in the local soil or lack of suitable environmental factors such as acidity/basicity of the soil.

On the contrary, the seeds were observed to grow very fast in different mixes of composts, mixed in different proportions with local soil (either ½ or ¼), and with composts mixed with 1% (wt/wt) biochar. In addition, the obtained fresh head weight of the cabbage was also higher. The variation in yield of fresh head weight of the cabbage among these treatments might be due to differences in their content of available nutrients (Getahun et al., 2012b). In this regard, the study of Dume et al. (2015) confirmed that the application of coffee husk biochar to acidic soils showed a better improvement in soil chemical properties (pH, electrical conductivity, cation exchange capacity, organic carbon/matter, total nitrogen, exchangeable cations and available phosphorous). The study of Maggen et al. (2017) also proved that a 2 wt% blending of biochar derived from the dry and solid fraction of pig manure with a poor soil affects positively plant growth and crops (dwarf beans), and worm (*Eisenia fetida*) survival and production. The same study also confirmed that by using the char, the available heavy metals are immobilized in the biochar and not leachable.Thus, the blending of biochar in soils not only has a positive effect on plant growth but also on the immobilization of heavy metal ions preventing their release towards ground water.

The results clearly indicate that using mature compost produced from C8 compost type (co-composting of 1/3rd coffee pulp, 1/3rd leaves of false banana (*Ensete ventricosum*), and 1/3rd soft dry woods) mixed with different proportions of local soil could result in a higher fresh head weight of the cabbage, which ranges from 422 ± 8 to 572 ± 10 g/kg of compost. This indicates that by mixing different types of composts in different ratios, by adding a lower amount of local soil, and with the addition of biochars, an optimum yield of the fresh head weight of the cabbage is obtained. In addition, when C8 compost type is mixed with local soil in 3:1 ratio, it could yield an optimum fresh head weight of the cabbage (572 ± 10 g/kg of compost). This might be due to the relatively higher concentration of total nitrogen in the C8 compost sample.

5.4 Conclusions

This study confirms that both coffee husk and pulp can be successfully composted alone or co-composted with other degradable fractions of source separated municipal solid waste in different proportions yielding very mature compost, which is stabilized and sanitized ensuring its optimum benefit for agriculture. From the results, the highest pH (in C3), EC (in C7), TN (in C7 and C8), available phosphorus (in C7), iron (in C7), potassium (in C5 and C7), C/N (in C3 and C1), and lowest OC and OM (in C3), and iron (in C1) were detected in these compost samples. The C/N ratio of matured compost samples is in the optimum range of < 25:1. The major contribution of matured compost samples of coffee husk and pulp is that they contributed the elements iron and potassium. Besides, they also contain other micronutrients which are essential to plant growth (which are required in much smaller amounts than the macronutrients) like, copper, manganese, zinc, nickel, and zinc. Furthermore, reasonable concentrations of heavy metals with no restrictions for use in agriculture were observed in all compost types and all are in the range of compost guidelines and standards set by Ethiopia, Belgium (for agriculture), the European Union, and the USA (for biosolids). In general, the results clearly indicate that using mature compost produced from C8 compost type (co-composting of $1/3^{rd}$ coffee pulp, $1/3^{rd}$ leaves of false banana (*Ensete ventricosum*), and $1/3^{rd}$ soft dry woods) mixed with different proportions of local soil could result in a higher fresh head weight of the cabbage. In addition, when C8 compost type is mixed with local soil in 3:1 ratio, it could yield an optimum fresh head weight of the cabbage (572 ± 10 g/kg of compost). This might be due to the relatively higher concentration of total nitrogen in the C8 compost sample. Furthermore, before producing and applying compost samples on soil, first of all, the chemistry of the local soil should be studied in detail. For example, if the pH of the soil is acidic, the produced compost should be slightly basic, otherwise, it can affect the local soil and hence it is the loss of energy, time and resources. Besides, if the soil lacks nutrients, for example, potassium, the produced compost should be rich enough in its content of potassium.

6. Valorization of coffee processing byproducts through pyrolysis

Abstract

The previous chapter describes the composting and co-composting potential of coffee pulp and husk in mixing with source separated municipal solid waste at the different ratio. This chapter investigates the pyrolysis of five different coffee waste fractions (coffee husk, pulp, silver skin, parchment and spent coffee) using non-catalytic processes. Thermogravimetric analysis (TGA) was performed for all samples (coffee husk, pulp, silver skin, parchment and spent coffee) in a nitrogen atmosphere from room temperature up to 550 °C (with a heating rate of 20 °C/min). After an isothermal period the atmosphere was changed to O_2 atmosphere and heating was continued to 900 °C (20 °C /min). The slow pyrolysis conversion conditions were applied using a vertical laboratory scale reactor. From the obtained bio-chars, activated carbon was prepared using a horizontal quartz tube reactor. More char and higher amounts of activated carbon could be produced from pyrolysis of coffee pulp compared to other coffee waste fractions. In contrast, more bio-oil is produced from silver skin and parchment pyrolysis. The FTIR spectrum of all coffee waste fractions (husk, spent coffee, silver skin, and parchment) indicates the presence of hydroxyl, C-H (SP^3 carbon), and C-O groups in all of them. The Thermal Desorption-Gas Chromatography/Mass Spectroscopy (TD-GC/MS) chromatogram results for coffee husk indicate that the three most abundant compounds in order of their relative abundance are palmitic acid, caffeine, and linolenic acid. The pyrolysis Gas Chromatography/Mass Spectroscopy chromatogram results for coffee husk also indicate that the three most abundant compounds (in order of their relative abundance) are phenol, methylphenol, and toluene. Furthermore, the Thermal Desorption-Gas Chromatography/Mass Spectroscopy (TD-GC/MS) chromatogram results for coffee pulp indicate that the three most abundant compounds (in order of their relative abundance) are hexadecanoic acid, 2-methoxy 4-vinylphenol, and stigmastan-3,5-diene. The pyrolysis Gas Chromatography/Mass Spectroscopy chromatogram results for coffee pulp also indicates that the three most abundant compounds are phenol, methylphenol, and toluene. In general, the identified compounds vary with the type of coffee fraction and the applied thermal desorption/pyrolysis

temperature. This might be because of the chemical composition (lignin, cellulose, and hemicelluloses content) of the coffee byproducts, and the amount as well as the duration of applied temperature.

Key words: Coffee waste, pyrolysis, bio-char, bio-oil, activation, Thermogravimetric analysis

6.1 Introduction

According to the detailed review conducted by Czajczyńska et al. (2017) different types of pyrolysis have been developed. These are fast, catalytic fast, intermediate, slow, and vacuum pyrolysis. Pyrolysis is an extremely complex process that results in three fractions: solid (char), liquid (pyrolysis oil) and gas. The yield and properties of these products are influenced by many factors such as the pyrolysis temperature, heating rate, vapor residence time and biomass input material (Raveendran et al., 1995; Demirbas, 2001).

Based on the heating rate, pyrolysis is categorized as slow, fast or flash pyrolysis. A low process temperature and long vapor residence times favor the production of char. High temperature and long vapor residence time increase the biomass conversion to gas. A moderate temperature and a short vapor residence time are the optimum process conditions for pyrolysis oil production (Demirbas and Arin, 2002; Demirbas, 2005). The pyrolysis oil can be easily stored and transported, and/or being directly used as a fuel imitative or for producing chemicals with high added value (Demirbas, 2004). However, pyrolysis oils are composed of different impurities (mixtures), high water/oxygen contents and hence have lower caloric values (20–25 MJ/kg, only about half of that of petroleum), and a low heating value, and they are strongly acidic and corrosive. All these problems limit its application as a fuel. Thus, further treatment and upgrading is needed in order to make pyrolysis oil a potential substitute for petroleum fuels (Xu and Lad, 2008).

Pyrolysis is one of the most developed thermochemical conversion techniques that can be applied to achieve thermal decomposition of biomass in the absence of oxygen to

derive biochar, bio-oil, and biogas (Abdelnur et al., 2013; Auta et al., 2014). The oil fraction has potential as a fuel and in other applications including greases, lubricants, resins, and in fine chemistry. Another application that has been studied is the use of pyrolysis oil blended with biodiesel to optimize the properties of pyrolysis oil as fuel (Figueiredo et al., 2009). The solid fraction (biochar) can also be used as a fuel, as well as in ceramics, components of building blocks, soil remediation and with suitable higher temperature treatment into activated carbon. Furthermore, it can be used on the farm as an excellent soil amender that can sequester carbon. Bio-char is highly absorbent and therefore increases the soil's ability to retain water, nutrients and agricultural chemicals, preventing water contamination and soil erosion. Soil application of biochar may enhance both soil quality and be an effective means of sequestering large amounts of carbon, thereby helping to mitigate global climate change through carbon sequestration. The gaseous fraction can also be used as a fuel (Romeiro et al., 2012).

The yield of each fraction depends on the applied pyrolysis conditions (temperature, heating rate, vapor residence time, etc.) and the properties of the biomass feedstock (Balat et al., 2009; Kılıç et al., 2014). In contrast to combustion and gasification, which produce energy in a form that is best used at the point of production (heat, steam or gas), (fast) pyrolysis converts biomass mainly into a liquid form that is easily storable and can be used when and where needed (Bridgwater, 2012). Pyrolysis gives ready-to-use fuels in an easy and safe way. Usually, gas and/or char are used as a source of energy because energy is the easiest product to utilize and sell. Liquid products from pyrolysis of MSW are very complex and usually contain water (Czajczyńska et al., 2017).

Therefore in this chapter, to answer the research gap indicated in section 1.6 of chapter 1, the valorization of coffee processing byproducts through pyrolysis is described in detail.

6.2 Methods and Materials

6.2.1 Specification of materials and sample preparation

The different fractions of coffee waste samples such as coffee husk (obtained when coffee berries are processed by the dry method), pulp (the first product obtained during wet coffee processing), parchment (obtained when washed coffee is dried and deshelled), silver skin (obtained during roasting coffee) and spent coffee ground (residue obtained during coffee brewing) were collected from Jimma zone, Oromiya region, Ethiopia. The spent coffee samples were collected from Jimma town residential houses, staff lounge and student cafeterias of Jimma University, Ethiopia. The parchment and silver skin samples were collected from dry coffee processing plants in Addis Ababa, Ethiopia. Representative raw samples were collected from coffee processing industries. The samples were packed with dried and cleaned HDPE plastics in order to avoid adsorption of moisture. Samples were homogenized and stored in a dry place until analysis.

Coffee waste samples particle size: The samples were air-dried, ground using a coffee blender (coffee grinder 'Seven 7 star', Germany) and passed through a 2 mm square-mesh sieve.

Type of pyrolysis: Preliminary TGA analysis was conducted and slow pyrolysis (a process that uses slower heating rates and biochar is usually the major product) was chosen as thermal treatment process. Slow pyrolysis has been used to enhance char production at low temperature and low heating rates (Jahirul et al., 2012). The liquid was collected in a glass bottle as indicated in figure 6.1. After cooling, the bio-oil was transferred to Schott Duran bottles and the biochar left in the reactor was collected in a plastic bottle for storage.

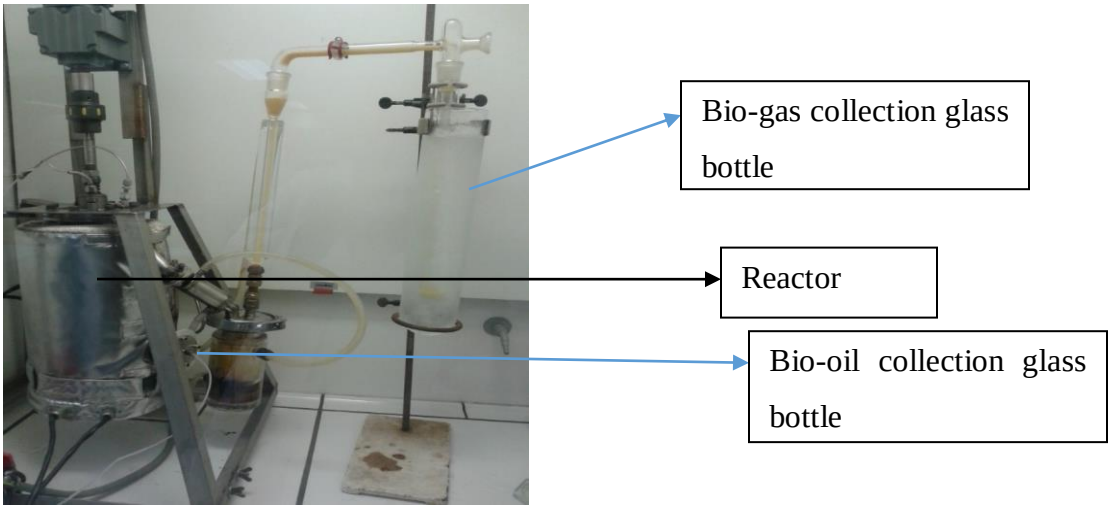


Fig. 6.1 Set up of the pyrolysis reactor

Pyrolysis reactor type: The pyrolysis reactor (vertical lab scale reactor) used for this study was made in the laboratory of Applied and Analytical Chemistry, University Hasselt, Belgium. The inside and outside of the reactor, as well as all materials used for pyrolysis, were cleaned thoroughly before and after the experiment. In addition, prior to the final pyrolysis of the samples, a preliminary pyrolysis trial was conducted.

For pyrolysis, samples were first pyrolyzed in an oxygen-free atmosphere (N_2) in the reactor. Afterwards, the reactor is sealed and placed under a stream of nitrogen; then, the reactor is heated with a rate of 10 ℃ /min to 500 ℃, and then hold isothermal for 1 h for a complete pyrolysis. The sample is continuously kept in motion by an Archimedes screw in order to achieve a uniform heat distribution (Rodríguez et al. 2017).

Sample characterization: Thermogravimetric analysis (TGA), semi-quantitative elemental analysis (XRF), and thermal desorption gas chromatography–mass spectrometry (GC/MS) and pyrolysis gas chromatography–mass spectrometry (GC/MS) after desorption were performed.

XRF analyses: A semi-quantitative elemental analysis was performed for husk, pulp and spent coffee samples) as such by XRF.

Thermogravimetric analysis (**TGA)**: TGA was performed to gain a better understanding of the pyrolytic behavior of all coffee waste samples (coffee husk, pulp, silver skin, parchment and spent coffee) in a nitrogen atmosphere from room temperature up to 550 °C (20 °C/min). After an isothermal period at 550 °C the atmosphere was changed to O_2 and heating was continued to 900 °C (20 °C/min).

TD-GC/MS and Pyrolysis GC/MS analysis: Thermal desorption (TD) GC/MS at 300 °C and pyrolysis GC/MS (550 °C) after desorption were applied for coffee husk and pulp samples.

FTIR (Fourier transform infrared) spectroscopy: FTIR spectra were obtained in attenuated total reflection (ATR) mode for coffee husk, spent coffee, silver skin, and parchment samples.

6.2.2 Activation of the biochar

For the activation of each bio-char, 8 gram of the biochar was placed into the activation reactor's tube (by covering the two sides of the tube with quartz wool and by adding the char in between this quartz wool). This tube is denoted as a quartz tube reactor (figure 6.2). Then this tube with the sample was inserted in a horizontal reactor (Nabertherm Germany). The biochar was heated up under a N_2 atmosphere to 800 °C at 20 °C /min. At 800 °C, the atmosphere was switched from nitrogen to water vapour (10 ml) to complete the activation process for 30 minutes (Rodríguez et al. 2017). Afterwards, it was cooled overnight in the reactor itself.

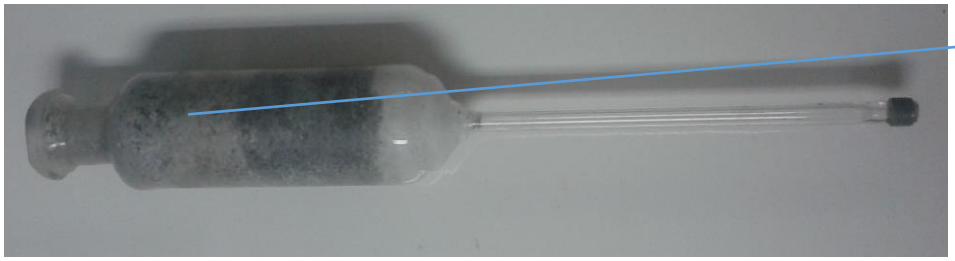


Fig. 6.2 Quartz tube reactor filled with char for the production of activated carbon in a horizontal oven set-up.

6.3 Results and Discussion

Before the biomass is pyrolyzed, using TGA, its characteristics (proximate analysis) are determined and the optimal pyrolysis temperature is calculated.

Thermogravimetric/Thermogravimetric Derivative (TG/TGD) curves for the different coffee waste fractions (husk, pulp, silver skin, parchment and spent coffee) are shown in figures 6.3a-e. The Thermogravimetric/Thermogravimetric Derivative (TG/TGD**)** results are presented in Table 6.1.

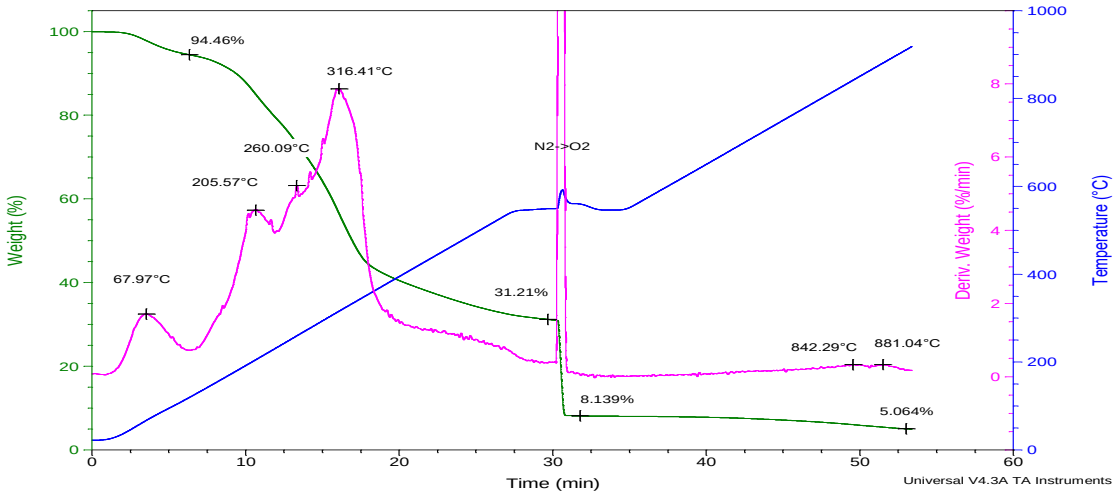


Fig. 6.3a: Thermogravimetric/Thermogravimetric Derivative (TG/TGD) curves of coffee husk

As indicated in Fig 6.3a, different peaks were observed. A peak at 260 °C is assigned to the decomposition of hemicelluloses, while a prominent DTG peak at 316 °C indicates the degradation of cellulose. In brief, the TG and DTG curves for husk showed two main regimes of weight loss, the lower temperature regime could be correlated with the decomposition of hemicelluloses and the initial stages of cellulose decomposition, while the upper-temperature regime correlated mainly with the later stages of cellulose decomposition.

In this regard, Al Chami et al. (2014) indicated that TG and DTG curves provide useful information on the yield of pyrolysis products (volatile and non-volatile). The same study indicated that the content of the major biomass structural components (cellulose, hemicelluloses, and lignin) can be estimated from the DTG curves since their decomposition is believed to proceed in specific temperature zones. In support of this, Williams and Besler (1996) and Yang et al. (2006) indicated that hemicellulose decomposition is typically reported to occur between 220 and 315 °C, while cellulose decomposes between 315 and 400 °C. Lignin decomposition, in contrast, usually occurs in a wide temperature interval (200 - 900 °C) and therefore is much more difficult to observe separately.

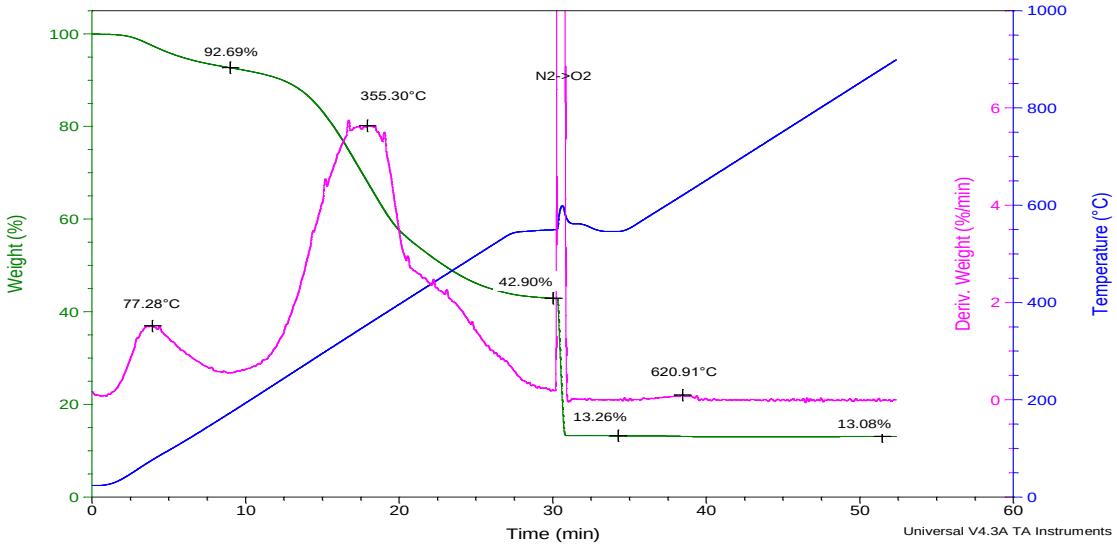


Fig. 6.3b: Thermogravimetric/Thermogravimetric Derivative (TG/TGD) curves of coffee pulp

As indicated in Fig 6.3b, only two peaks were observed and a prominent DTG peak at 355 °C indicates the degradation of cellulose. This result agrees with the previous reports of Williams and Besler (1996) and Yang et al. (2006).

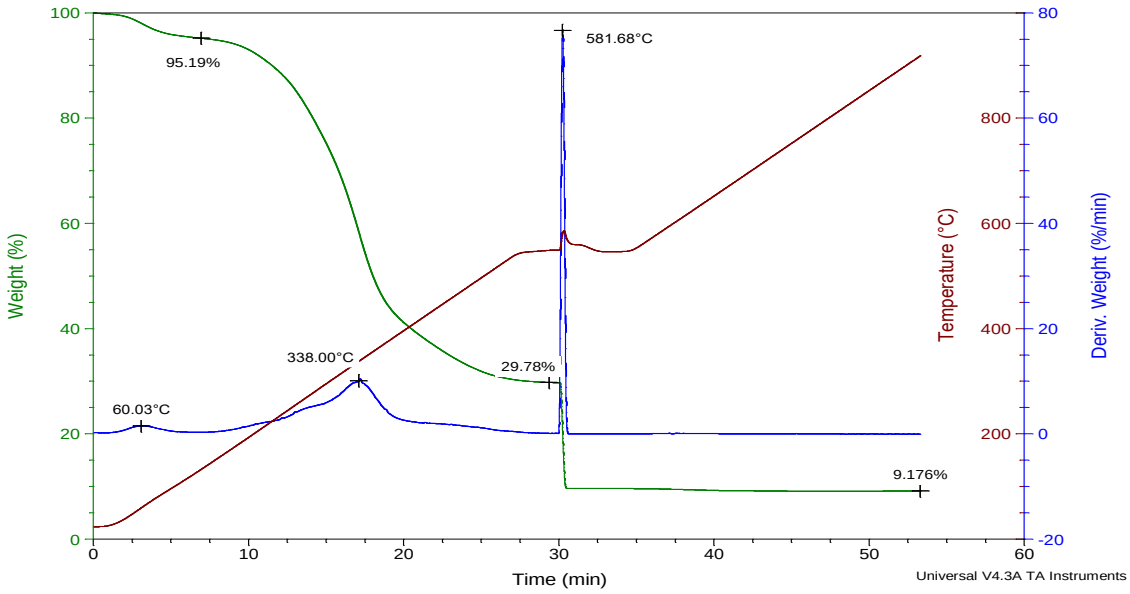


Fig. 6.3c: Thermogravimetric/Thermogravimetric Derivative (TG/TGD) curves of coffee silver skin

As shown in Fig 6.3c, a dominant DTG peak at 338 °C indicates the degradation of cellulose; this is supported by previous reports (Williams and Besler, 1996; and Yang et al., 2006).

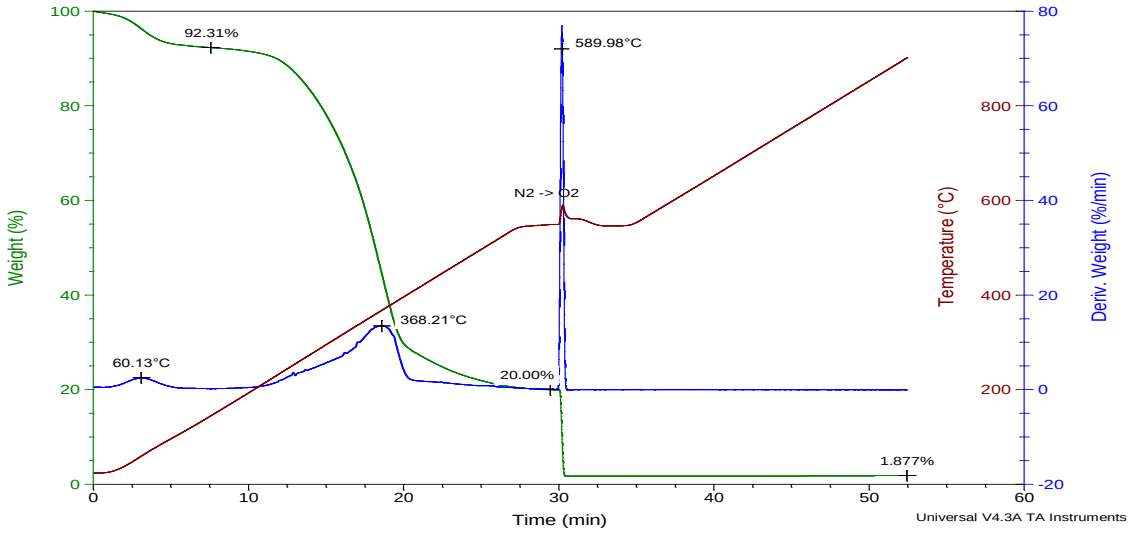


Fig. 6.3d: Thermogravimetric/Thermogravimetric Derivative (TG/TGD) curves of coffee parchment

As indicated in Fig 6.3d, the Thermogravimetric/Thermogravimetric Derivative (TG/TGD) curve of parchment coffee is very similar to the silver skin DTG curve. Hence, only two peaks were observed and a dominant DTG peak at 368 °C indicates the degradation of cellulose. This result is supported by the literature (Williams and Besler, 1996; Yang et al., 2006). The dominant DTG peak in the coffee pulp, silver skin and parchment coffee is more indicative of the high cellulose content than the other fractions (hemicelluloses and lignin).

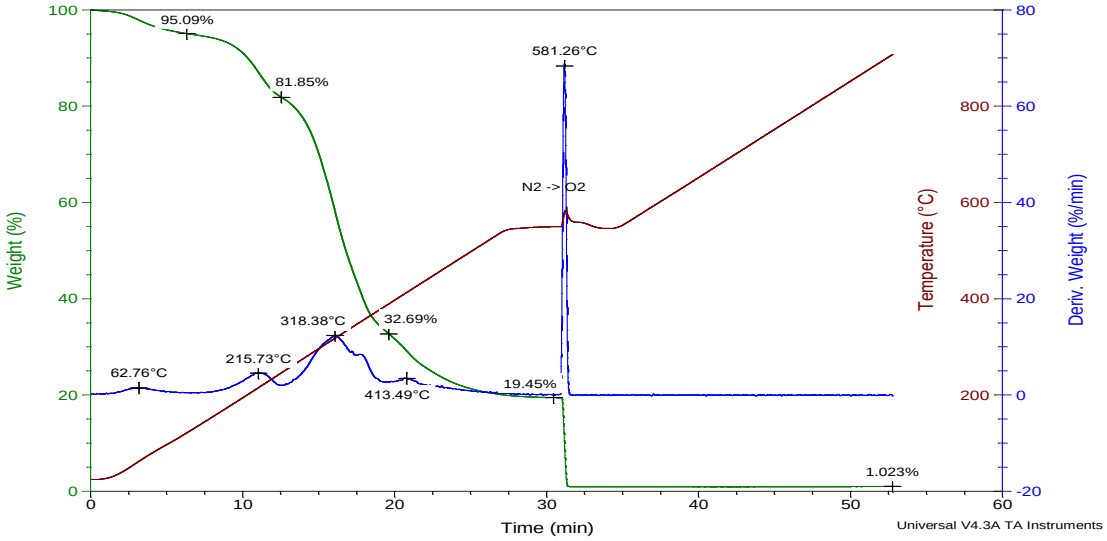


Fig. 6.3e: Thermogravimetric/Thermogravimetric Derivative (TG/TGD) curves of spent coffee

As shown in Fig 6.3e, similar to the case of coffee husk, the Thermogravimetric/Thermogravimetric Derivative curves for spent coffee showed different peaks. Furthermore, similar to the case of coffee husk, the TG and DTG curves for spent coffee show two main regimes of weight loss, the lower temperature regime (216 to 318 °C) could be correlated with the decomposition of hemicelluloses and the initial stages of cellulose decomposition, while the upper-temperature regime (414 °C) correlated mainly with the later stages of cellulose decomposition. In particular, as indicated in Fig 6.3e, a prominent DTG peak at 318 °C indicates the degradation of cellulose.

In general, the TG/DTG-curves showed that most of the decomposition reactions were finished before about 550 °C. Therefore, based on the above TG/TGD findings a pyrolysis temperature of 550 °C was chosen. Furthermore, the TG/DTG curves in Figure 6.3a-e clearly indicated that cellulose is the typical component of all coffee waste fractions (husk, pulp, silver skin, parchment and spent coffee). The TGA results of the different coffee waste fractions (spent coffee, husk, pulp, parchment, and silver skin) are summarized in Table 6.1.

Table 6.1: Thermogravimetric/Thermogravimetric Derivative (TG/TGD) results

Sample	Mass loss					
	RT-110 °C	110-330 °C	350-550 °C	Fixed C	Ash residue	
					600 °C	900 °C
Husk	5.5	49.5	13.8	18.1	8.1	5.0
Coffee pulp	7.3	12.7	37.1	29.6	13.3	13.1
Silver skin	4.8	40.2	25.2	20.6	9.2	9.2
Parchment	8.7	36.3	35.0	18.1	1.9	1.9
Spent coffee	4.9	41.1	34.55	18.45	1.0	1.0

The initial mass loss can be assigned to moisture (from room temperature (RT) - 110 °C) for all coffee waste products. The additional mass loss occurs in a more complex stepwise process for husk and spent coffee with the same maximum evolution temperature at around 317 °C compared to the other fractions. The degradation process can be considered as a combination of thermal desorption but mainly by pyrolytic degradation of the different organic parts. During silver skin, pulp and parchment pyrolysis, the temperature for thermal cracking is shifted to the enhanced temperature of 338 °C, 355 °C and 368 °C, respectively (See Figures 6.3a-e). The volatile organic matter is the highest for spent coffee (75.6%) and parchment (71.3%), followed by silver skin (65.4%) and husk (63.3%) and the lowest amount is measured for the pulp fraction (49.8%). The fixed carbon content can be determined after switching to an oxidative atmosphere at 550 °C using oxygen with CO_2 releases as the result of combustion of carbonized residue.

The fixed carbon content is the highest for coffee pulp (29.6%), followed by silver skin (20.6%), and almost equally spent coffee (18.4%), husk (18.1%), and parchment (18.1%). The amounts of volatiles and fixed carbon can determine the yields of obtained char after pyrolysis. The ash residue at 900 °C, which is a measure for the inorganic fraction, are

respectively 13 % (pulp), 9 % (silver skin), 5% (husk), parchment (2%) and the lowest for spent coffee (1%). In the case of husk small amounts of $CaCO_3$ could be present (3%), not found in the other fractions. Parchment and spent coffee have only a minor mineral fraction and have also the largest mass loss in the temperature of about 550 °C.

As indicated in Table 6.2, silver skin and parchment yield more bio-oil than the other fractions. Previously, the study of Deligiannis et al. (2011) reported that the oil content of spent coffee contained 15% on the dry weight basis. From the study of Kan et al. (2013), the GC-MS analysis revealed that pyrolysis of spent coffee in the presence of a catalyst produced a lower amount of bio-oil and a more homogeneous distribution of organic compounds in the bio-oil than in the case without catalysts.

Table 6.2: Amount of bio-char, bio-oil and bio-gas produced from different coffee waste fractions

Pyrolyzed	**Product yield**		
Sample	**Clear filtrate bio-oil (%)**	**Bio-char (%)**	**Bio-gas (%)**
Spent coffee	23 ± 5	36 ± 4	41 ± 3
Husk	22 ± 3	39 ± 5	39 ± 2
Pulp	18 ± 2	52 ± 1	30 ± 3
Parchment	32 ± 4	27 ± 6	41 ± 4
Silver skin	33 ± 5	34 ± 2	33 ± 5

The highest amount of biochar was obtained from coffee pulp fraction; the lowest amount resulted from parchment. The amount of biogas obtained from both spent coffee and parchment is comparable. These differences in the yield might be due to the difference in the chemical composition of each coffee waste fraction (Elias, 1979; Mussatto et al., 2011). The study of Al Chami et al. (2014) also reported 33% oil yield from the pyrolysis of harvested sorghum bicolor biomass using slow pyrolysis. In general, the values reported in Table 6.2

are in agreement with the values reported by Jahirul et al. (2012) for slow pyrolysis in which the product yields are expected to be 30% oil, 35% char and 35% gas.

As indicated in Figure 6.4, higher activated carbon is produced from pyrolysis of coffee pulp than the other fractions of coffee waste, with the lowest yield for husk. In this regard, the study of Gonçalves et al. (2013) reported that coffee pulp is a very interesting precursor for activated carbon preparation and it is a potential adsorbent for organic contaminants in aqueous solution. The study of Reffas et al. (2010) indicated that the activated carbons prepared from spent coffee were compared to a commercial activated carbon towards the adsorption of methylene blue and "Nylosan Red N-2RBL", a cationic and anionic (azo) dye.

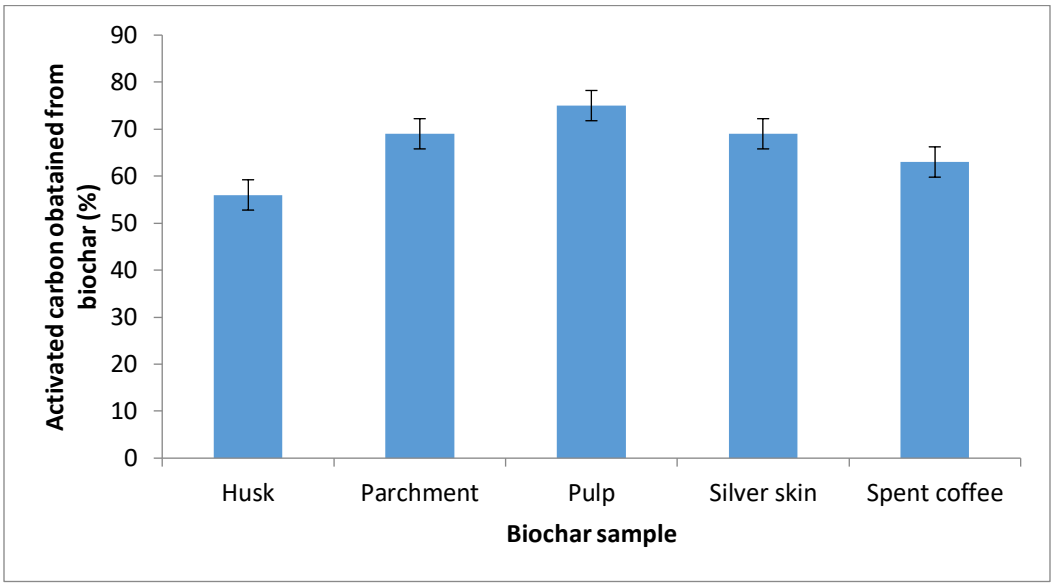


Fig. 6.4. Activated carbon obtained from biochar of different coffee waste fractions

Boonamnuayvitaya et al. (2005) also reported that six types of activated carbons could be prepared from coffee residues by varying activating agents (such as $ZnCl_2$, N_2, CO_2, and steam). The study of Dume et al. (2015) indicated that addition of biochar which is prepared from coffee husk and corn cob to acidic soils have the potential to improve the

physicochemical properties of acidic soil, soil fertility, and crop yield. Furthermore, the study of Rodríguez et al. (2017) confirmed that spent coffee and coffee husk (obtained from Jimma Ethiopia), pyrolyzed, and then activated show a high affinity for Ni(II) adsorption. The same study also confirmed that the sorption efficiency was higher for husk activated carbon whereby it removes > 94% of Ni (II), achieving safe discharge concentration values.

From the experiments, it was observed that the weight of the muddy part (solid part of the bio-oil) of the condensate decreased in the order spent coffee > pulp > husk >> parchment ~ silver skin. Parchment and silver skin have no residue at all, although there is a little (insignificant) sediment at the bottom of the parchment. Silver skin is free of any residue (100%). It was observed that the pyrolyzed coffee waste samples produced a bio-oil having different colors and different amount of smoke production. The results are indicated in Table 6.3.

Table 6.3: Characteristics of bio-oil produced from the different coffee waste fractions

Sample	**Color**
Spent coffee	Color of coca-cola (deep black)
Husk	Color of yellow label tea (common tea)
Pulp	Color of yellow label tea (common tea)
Parchment	Similar to the color of spent coffee but not deep black as that of spent coffee (light black)
Silver skin	Similar to the color of spent coffee but not deep black as that of spent coffee (light black). That is, similar to the color of parchment.

From the experiments, it was observed that pyrolysis of silver skin and parchment is different from the other coffee waste fractions as more smoke was emitted (with pungent smell and abundant gas emission). However, the smoke emission released during pyrolysis of silver skin is lower than the pyrolysis of parchment.

Fourier Transform Infrared Spectroscopy (FTIR spectra) of the samples (husk, spent coffee, silver skin, and parchment) is shown in figure 6.5a-d.

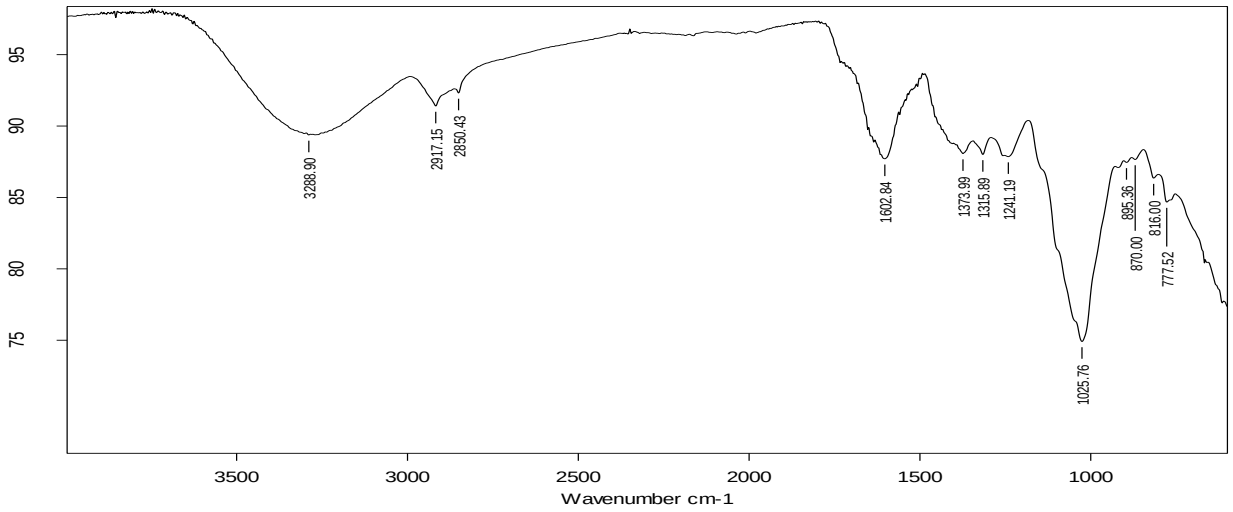


Fig. 6.5a: FTIR spectrum of coffee husk

As indicated in figure 6.5a, the IR spectrum of husk reveals the presence of aromatics (1600 cm^{-1}) and hydroxyl (3300 cm^{-1}) functional groups. The intense absorption band at 1025 cm^{-1} can be assigned to C-O vibrations. The IR spectrum of spent coffee (figure 6.5b) shows the presence of carbonyl groups at 1704 cm^{-1} and secondary amide (peptide) bands at 1650 and 1540 cm^{-1}. The weak absorption peak at 3010 cm^{-1} can be assigned to Csp_2-H vibrations. The CH_2 rocking vibration (719 cm^{-1}) confirms the presence of long carbon chains. The IR spectrum of silver skin (figure 6.5c) can be related to an enhanced content of peptide bonds (1650 and 1540 cm^{-1}) together with esters (1739 cm^{-1}) and acids (1700 cm^{-1}). The IR spectrum of parchment (figure 6.5d) is similar to the IR pattern of silver skin apart for the absence of acid groups.

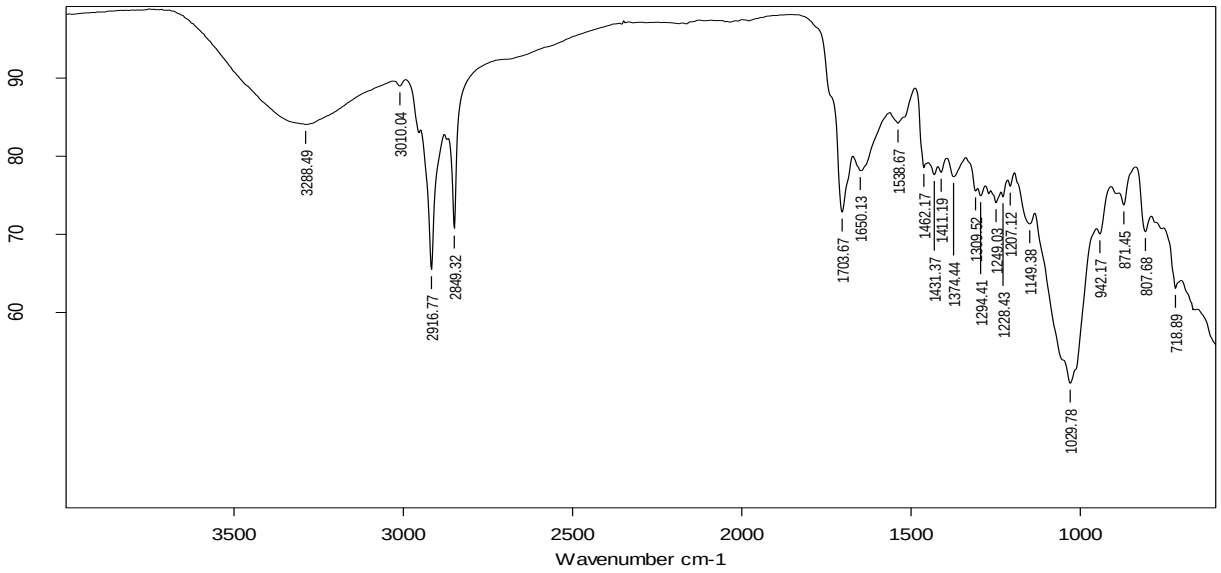


Fig. 6.5b: FTIR spectrum of spent coffee

A very similar FTIR spectrum was observed by Klug et al. (2015) and (Li et al., 2014) from pyrolysis oil of coffee ground samples from Peru. This study reported the presence of phenols, alcohols, alkanes, aldehydes, aromatic rings with various types of substituents. Furthermore, similar observations were reported by the study of Vardon et al. (2013) on spent coffee grounds.

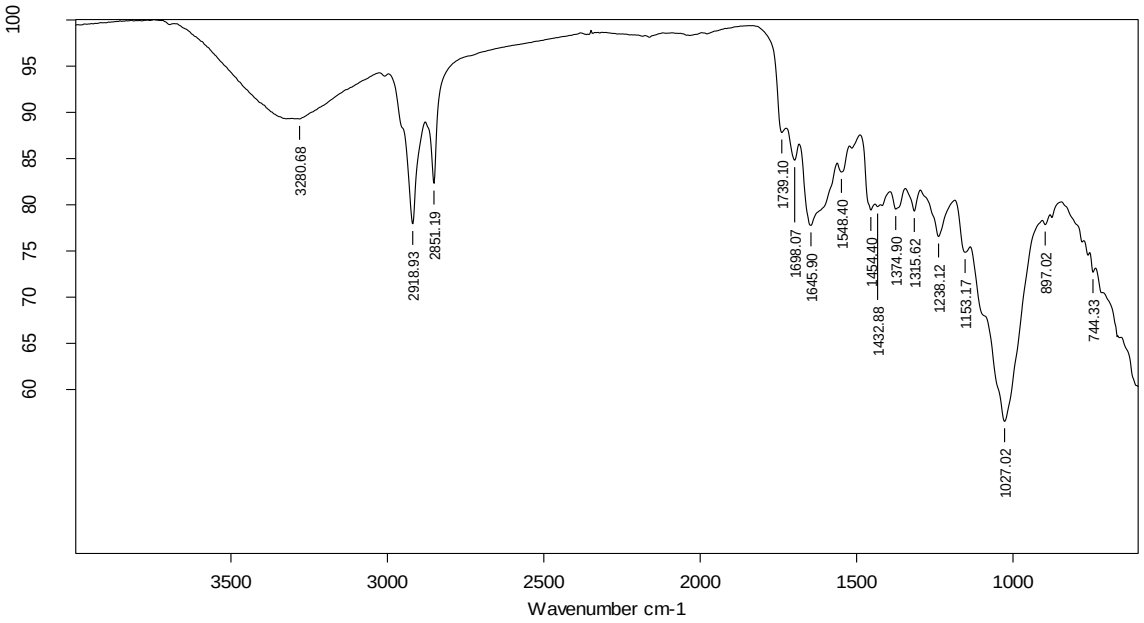


Fig. 6.5c: FTIR spectrum of coffee silver skin

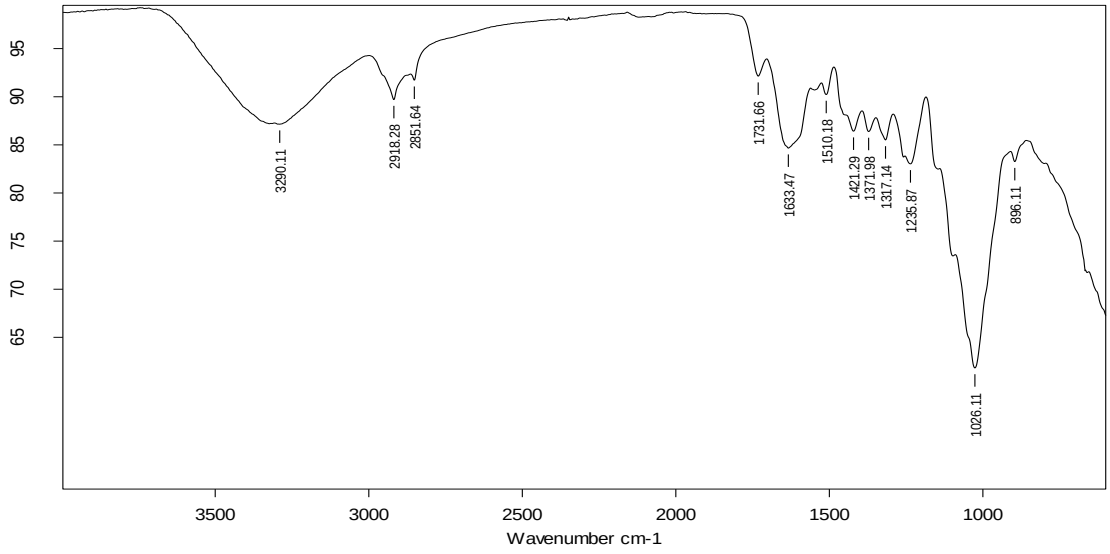


Fig. 6.5d: FTIR spectrum of parchment

In general, as shown in the figures 6.5a-d, for all these coffee waste fractions (husk, spent coffee, silver skin, and parchment), the absorption band at 3288 cm^{-1}, 2916-2850 cm^{-1},

and 1025-1029 cm^{-1} indicated the presence of hydroxyl, C-H (SP^3 carbon), and C-O groups, respectively.

Semi-quantitative X-ray fluorescence (XRF) results for husk, pulp and spent coffee, expressed as oxide and in element form, in wt % are summarized in Table 6.4.

Table 6.4: Semi-quantitative XRF results

	Husk		**Pulp**		**Spent coffee**	
Formula	**Conc (%)**	**Element (%)**	**Conc (%)**	**Element (%)**	**Conc (%)**	**Element (%)**
$C_6H_{10}O_5$	91.79		86.7		98.9	
MgO	0.21	0.13	0.425	0.26	0.15	0.09
Al_2O_3	0.18	0.09	3.01	1.59	0.02	0.01
SiO_2	0.38	0.18	4.13	1.93	0.05	0.02
P_2O_5	0.41	0.18	0.46	0.2	0.14	0.06
SO_3	0.51	0.2	0.76	0.3	0.2	0.08
Cl	0.07	0.07	0.01	0.01	-	-
K_2O	5.43	4.51	0.39	0.33	0.31	0.26
CaO	0.76	0.54	2.16	1.54	0.11	0.08
TiO_2	0.02	0.01	0.2	0.12	trace	trace
MnO	0.01	0.01	0.05	0.04	0.002	0.0015
Fe_2O_3	0.12	0.08	1.66	1.16	0.019	0.013
CuO	0.003	0.003	0.01	0.004	0.002	0.0014
ZnO	0.002	0.002	0.01	0.005	0.001	0.0007
Rb_2O	0.01	0.01	trace	trace	trace	trace
SrO	trace	trace	0.011	0.009	trace	trace

As indicated in Table 6.4, K is the major element in the coffee husk. Minor elements are Mg, Ca, Al, Si, S, P, and Fe. Detected trace elements are Mn, Ti, Cl, Cu, Zn, and Rb. Ca, Al, Si, and Fe are the major elements in coffee pulp. Minor elements are Mg, P, S, K, and Ti. Trace elements found are Cl, Mn, Cu, Zn, and Sr. For spent coffee the elemental distribution is similar to the other samples but in lower concentrations. The presence of K, Ca and transition metals (Fe, Ni, Cu, Mn, Zn, and Ti) in the pyrolyzed sample of coffee ground was reported by Klug et al. (2015). The higher amount of K in coffee husk was confirmed by the study of Rodríguez et al. (2017). This result agrees with literature data.

Thermal desorption-Gas Chromatography/Mass Spectroscopy (TD-GC/MS) and pyrolysis GC/MS chromatograms for husk and pulp are indicated in figures 6.6a-d.

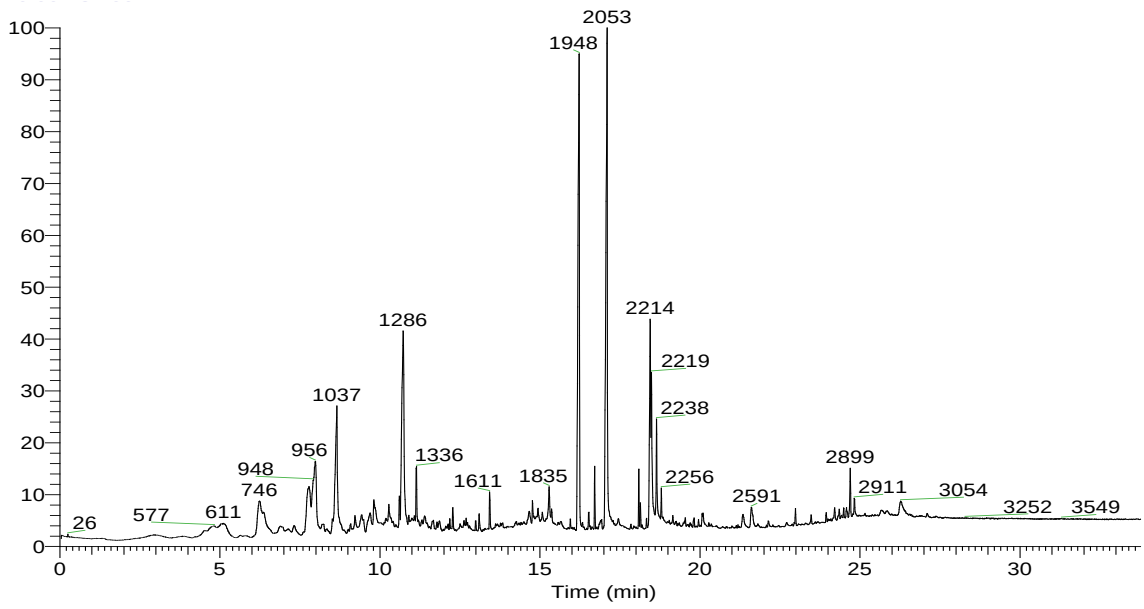


Fig. 6.6a: TD-GC/MS chromatogram of coffee husk

The Thermal Desorption-Gas Chromatography/Mass Spectroscopy (TD-GC/MS) chromatogram results for coffee husk indicates the most abundant compounds in order of their relative abundance (dominance). These are palmitic acid, caffeine, linolenic acid, 1,4-

benzenediol, oleic acid, 3-hydroxy-2,3-dihydromaltol, stearic acid, 2,6-dimethoxyphenol, stigmastan-3,5-diene, hexadecaneamide, 4-((1E)-3-hydroxy-1-propenyl)-2-methoxyphenol, 3,5-dimethoxy acetophenone, phenol, and sitosterol. The list of all identified compounds is indicated in Appendix (Table A2).

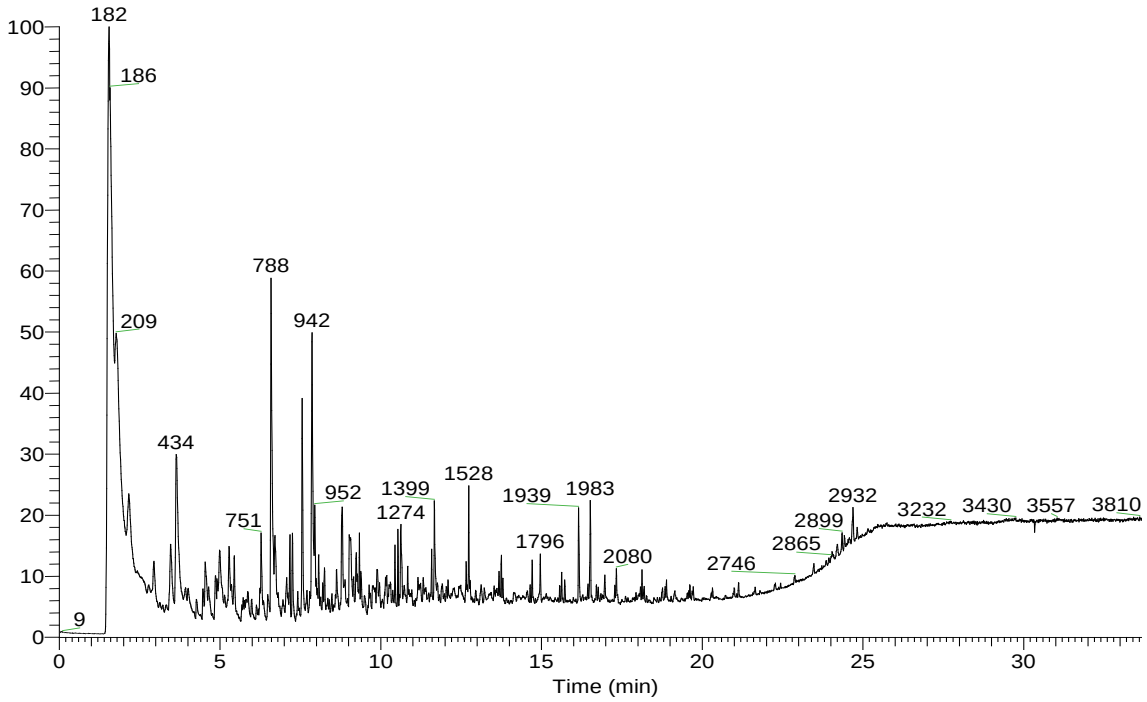


Fig. 6.6b: Pyrolysis GC/MS chromatogram of coffee husk

The pyrolysis Gas Chromatography/Mass Spectroscopy chromatogram results for coffee husk indicates the most abundant compounds in order of their relative abundance. These are phenol, methylphenol, toluene, pentadecane, 4-methoxyphenol, tetradecane, hexadecanenitrile, caffeine, indol, and stigmastan-3,5-diene. The list of all identified compounds is indicated in Appendix (Table A3).

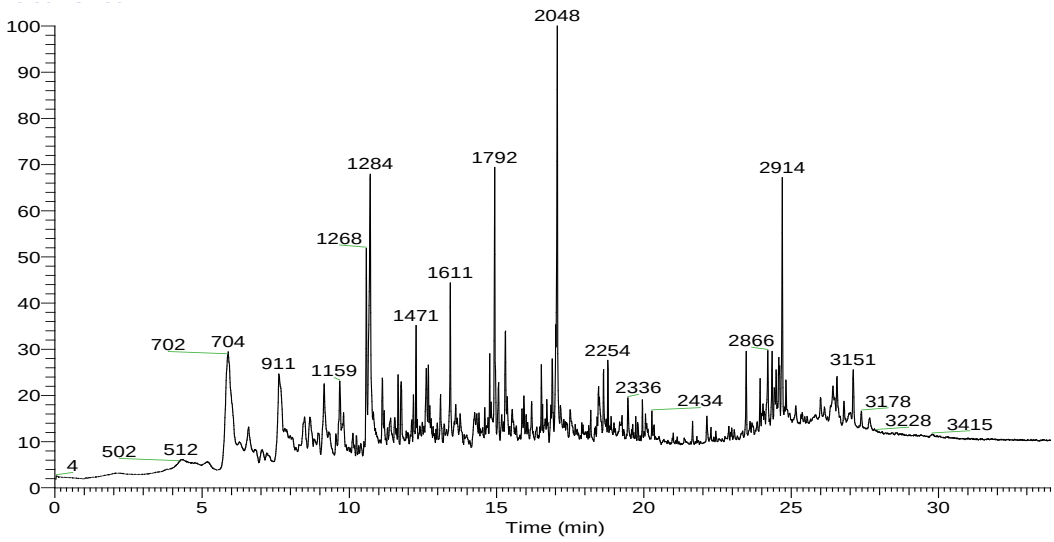


Fig. 6.6c: TD-GC/MS chromatogram of coffee pulp

The Thermal Desorption-Gas Chromatography/Mass Spectroscopy (TD-GC/MS) chromatogram results for coffee pulp indicates the most abundant compounds in order of their relative abundance. These are hexadecanoic acid, 2-methoxy 4-vinylphenol, stigmastan-3,5-diene, indol, dimethoxyacetophenone, isoeugenol, phenol, ergost-5-en-3-ol acetate, hexadecane amide, stigmast-4-en-3-on, and 2,3-dihydrobenzofuran. The list of all identified compounds is indicated in Appendix (Table A4).

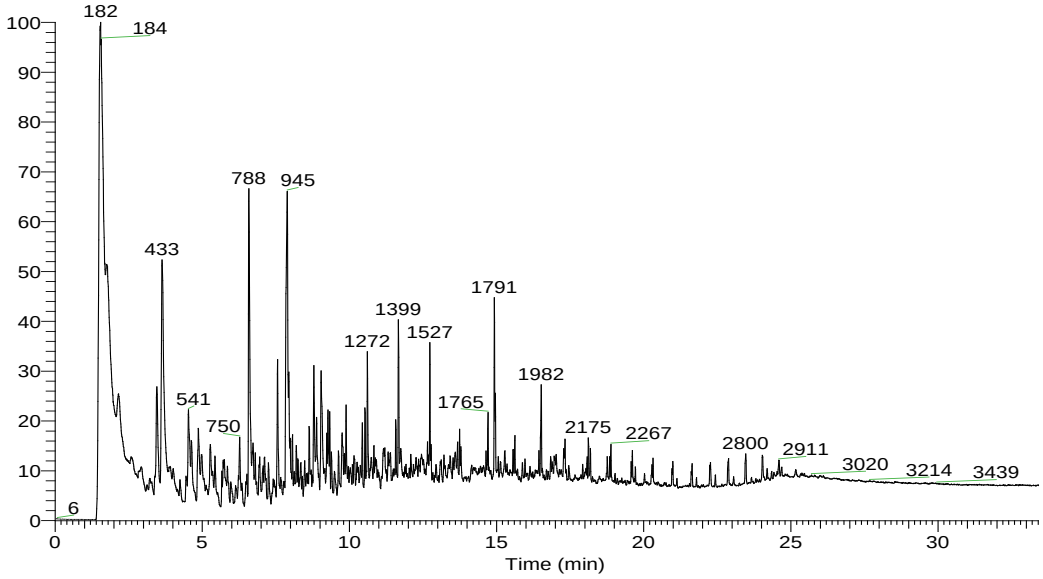


Fig. 6.6d: Pyrolysis GC/MS chromatogram of coffee pulp

The pyrolysis Gas Chromatography/Mass Spectroscopy (GC/MS) chromatogram results for coffee pulp indicates the most abundant compounds in order of their relative abundance. These are phenol, methylphenol, toluene, tetradecane, pentadecane, indol, hexadecane nitrile, 3-methylpyrrole, heptadecane, 3-methyl 2-cyclopenten-1-one, heneicosane, and docosane. The list of all identified compounds is indicated in Appendix (Table A5).

The list of the most prominent 10 identified compounds from each of TD-GC/MS chromatogram and pyrolysis GC/MS chromatogram of coffee husk and pulp is summarized in Table 6.5.

Table 6.5. List of the prominent 10 identified compounds from TD-GC/MS and pyrolysis GC/MS chromatogram of coffee husk and pulp

S.No.	Husk		Pulp	
	TD-GC/MS	**Pyrolysis GC-MS**	**TD-GC/MS**	**Pyrolysis GC-MS**
1.	Palmitic acid	Phenol	Hexadecanoic acid	Phenol
2.	Caffeine	Methylphenol	2-methoxy 4-vinylphenol	Methylphenol
3.	Linolenic acid	Toluene	Stigmastan-3,5-diene	Toluene
4.	1,4-benzenediol	Pentadecane	Indol	Tetradecane
5.	Oleic acid	4-methoxyphenol	Dimethoxyacetophenone	Pentadecane
6.	3-hydroxy-2,3-dihydromaltol	Tetradecane	Isoeugenol	Indol
7.	Stearic acid	Hexadecanenitrile	Phenol	Hexadecane nitrile
8.	2,6-dimethoxyphenol	Caffeine	Ergost-5-en-3-ol acetate	3-methylpyrrole
9.	Stigmastan-3,5-diene	Indol	Hexadecane amide	Heptadecane
10.	Hexadecaneamide	Stigmastan-3,5-diene	Stigmast-4-en-3-on	3-methyl 2-cyclopenten-1-one

From the TD-GC/MS and pyrolysis GC/MS chromatogram of coffee husk and pulp indicated in Table 6.5, it is possible to observe that even though there are minor similarities among the identified compounds (example, stigmastan-3,5-diene, phenol, indol, hexadecaneamide, tetradecane, pentadecane, toluene, and methylphenol), most of the compounds are different in the different cases. This might be because of the differences in their chemical composition (content of cellulose. hemicellulose, and lignin) and the applied thermal/pyrolytic temperature of the different fractions of coffee byproducts.

As an example, the current selling price of 10 gram of palmitic acid (purity > 98%), 1 liter of phenol (≥ 96 %), and 1 kg of methylphenol (≥ 99%) is 52.30, 46.40, and 68.25 euro, respectively (reference price from Sigma Aldrich). The identified compounds indicated in Table 6.5 indicated that there is a potential to use coffee byprodutcs as a resource for the manufacture of different products and this clearly gives the possibility of saving the aforementioned expenses for the purchase of different industrial chemicals and reagents. The implication is that, since coffee husk and pulp are available abundantly, they can be recycled. Furthermore, the overall implication is that there is a great potential to valorize each of the fractions of coffee byproducts as beneficial resources for the manufacture of different compounds.

In general, in addition to the list of compounds presented in Figures 6.6a-d, the abundance of all coffee waste fractions (particularly husk, pulp, parchment, and spent coffee) and the yield that could be obtained (for example, biochar, bio-oil and biogas), pyrolysis of the different coffee byproducts offers potential as a valuable feedstock for different purposes (economically, environmentally and in terms of saving the public health).

6.4 Conclusions

The results clearly indicated that slow temperature pyrolysis of coffee waste fractions can be one of the alternatives for the sustainable management of coffee byproducts. In particular, the coffee waste fractions silver skin and parchment were found to yield higher bio-oil yield than the other coffee waste fractions. Coffee pulp yields higher amount of biochar and activated carbon. This, in turn, implies that the coffee waste fractions (byproducts) can be recycled if there is proper management of coffee waste fractions among different stakeholders. In general, it can be concluded that valorization of coffee waste fractions via non-catalytic pyrolysis is a promising alternative to reclaim biochar, bio-oil, biogas, activated carbon and generation of compounds of added value, for example, the Thermal Desorption-Gas Chromatography/Mass Spectroscopy (TD-GC/MS) and pyrolysis Gas Chromatography/Mass Spectroscopy chromatogram results for coffee husk and pulp indicates the generation of compounds of added value. For example, palmitic acid, caffeine, linolenic acid, 1,4-benzenediol, oleic acid, phenol, methylphenol, toluene, pentadecane; hexadecanoic acid, 2-methoxy 4-vinylphenol, stigmastan-3,5-diene, indol, dimethoxyacetophenone, and tetradecane are some of the most abundant compounds. In summary, the results indicate that pyrolysis is one of the promising alternatives to reclaim compounds of interest value from different coffee waste fractions. Moreover, further research is needed to evaluate the effect of biochar and activated carbon prepared from different fractions of coffee waste for treatment of wastewater from tanneries, textile industry, and others.

7. General conclusions and recommendations for further research

7.1 General discussion and conclusions

Coffee is one of the world's most prominent agricultural products, mainly used as a beverage. It is a highly popular product, consumed by millions of people every day and it is the second largest traded commodity in the world after petroleum. However, it generates a large amount of coffee by-products/residues during processing from fruit to cup. Coffee waste products and by-products produced during coffee berry processing constitute a source of severe contamination and pose serious environmental problems in coffee producing countries. Thus, unless treated, coffee waste, pollutes water sources, damages aquatic ecosystems, and threatens public health and wildlife, which offsets the economic benefits accrued from coffee production. In general, it is important to consider that these byproducts can contribute to environmental problems if not disposed of properly.

For instance, all wet coffee processing industries in Ethiopia are not re-using the water once used for depulping and fermentation. Thus, all the generated wastewater is directly released to the downstream water bodies and sometimes in the disposal pits. Besides, most of the wet coffee processing industries are using either the wet method or dry coffee processing method, and semi-washed coffee processing is not given due attention. Thus, the downstream impact of these wet coffee processing industries on the downstream waterbodies and the ecological system is significant. Furthermore, coffee processing industries burn the dried coffee pulp and husk. This, in turn, contributes to air pollution. Thus, there is a need to find alternative uses for these residues. In this study, the potential for valorization of coffee byproducts via biomass conversion technologies (fermentation, pervaporation, composting and pyrolysis of coffee waste fractions) was evaluated. The major key findings are indicated as follows:

1) During the wet coffee processing, the variation in soaking time of coffee beans, fermentation of the coffee pulp, and absence of appropriate treatment facilities were the major factors associated with the magnitude of the water pollutant parameters

released by the coffee processing plants. In general, the measured values of effluent parameters significantly deviate from both the Ethiopian-EPA and US-EPA guidelines, with a concentration of most of the measured physicochemical parameters higher than the recommended values. Thus, water bodies and ecosystems located downstream of the traditional wet coffee processing plants are at an alarming risk of ecological disruption.

2) The results of the investigation via fermentation and pervaporation also demonstrate that coffee husk, spent coffee, and coffee pulp can be used as an alternative substrate for ethanol production, in comparison to different biomass resources. In particular, coffee husk hydrolysis using acid and cellulolytic hydrolysis and fermentation with lignocellulosic yeast GSE16-T18 followed by pervaporation was found to be the best process for producing the highest ethanol yield compared to the other fractions of coffee waste samples.
3) The results of the composting study indicate that coffee husk and pulp can be composted alone or co-composted with source separated municipal solid waste (SSMSW) yielding very mature and stable compost with good quality, which is in the range of compost quality standards/guidelines set by different countries. It was confirmed that the addition of $1/4^{th}$ of local soil (wt/wt) on C8 compost type (the mixture of compost produced from 1/3 coffee pulp, 1/3 false banana leaves (*Ensete ventricosum*), and 1/3 soft dry woods), yields the optimum fresh head weight of the cabbage among all field trials. This might be due to the relatively higher concentration of total nitrogen in the C8 compost sample.
4) The pyrolysis results clearly indicated that slow temperature pyrolysis of coffee waste fractions can be one of the alternatives for the sustainable management of coffee byproducts. In particular, the coffee waste fractions silver skin and parchment were found to yield better bio-oil yield than the other coffee waste fractions. Besides, coffee pulp is ranked the best alternative of all coffee waste fractions yielding higher amount of biochar and activated carbon. In general, it can be concluded that valorization of coffee waste fractions via non-catalytic pyrolysis is a promising alternative to reclaim bio-char, bio-oil, biogas, activated carbon and generation of

compounds of added value, for example, the Thermal Desorption-Gas Chromatography/Mass Spectroscopy (TD-GC/MS) and pyrolysis Gas Chromatography/Mass Spectroscopy chromatogram results for coffee husk and pulp indicates that palmitic acid, caffeine, linolenic acid, phenol, methylphenol, toluene, hexadecanoic acid, 2-methoxy 4-vinylphenol, and stigmastan-3,5-diene are some of the most prominent compounds among the identified long list of compounds.

5) The results on the concentration of bioethanol by pervaporation of the fermentation broth of dried coffee pulp indicate that pervaporation needs to be further improved by enhancing the ethanol selectivity. Furthermore, it is concluded that to get pure bioethanol from coffee waste pervaporation, hydrophobic pervaporation (PV) is not enough. The simulation results also showed that hydrophobic pervaporation is theoretically the best option, but at present, a complete separation can be only achieved with the hydrophilic membranes combined with distillation in hybrid configuration (particularly working in vapor permeation mode).
6) In general, it is concluded that the results from the fermentation, pervaporation, composting and pyrolysis of coffee waste fractions indicate that coffee byproducts can be a suitable candidate for resource recovery in view of sustainable coffee production.

7.2 Recommendations for further research

The results from the hydrolysis, fermentation, pervaporation, composting and co-composting as well as pyrolysis of coffee waste fractions study indicate that coffee byproducts can be a suitable candidate for resource recovery in view of sustainable coffee production. In addition to the production of the valuable products (bioethanol, bio-oil, biochar, biogas, activated carbon, mature and stable compost) from coffee waste fractions, this thesis recommends the following further activities to be done for better achievement of the desired target as well as to make the overall coffee production sustainable:

1. The polluting potential of the wet coffee processing factories is enormous at locations below effluent discharge points even after stabilization in a disposal pit, indicating the deterioration of water quality in downstream locations where untreated coffee effluent was discharged into the water sources. Thus, in order to comply with the environmental regulations and achieve a restoration of the environment, it is necessary to find an economical and easily adaptable technology for the treatment of coffee wastewater. For instance, the technology that can reduce the amount of water consumption for washing, depulping, and fermentation, which in turn can assist in reducing the amount of wastewater.
2. Using the semi-washed method, aspects both the washed and unwashed methods are combined. In this process, the out skins are removed, but the pulp is allowed to remain and dry in the sun. Once the drying process is complete, often the pulp is wet and then the beans are removed just like they are in the dry process. That means coffee fruits are washed and sorted as in the washed method. But, they are not placed in fermentation tanks instead they are set out to dry. Therefore, by using the semi-washed processing, it is possible to reduce the water consumption and allows re-using of the wastewater. This, in turn, reduces the environmental burden and health problems of the local community. Thus, the government is expected to encourage wet coffee processing industry owners and local communities to follow and implement the semi-washed coffee processing method to save the environment and public health from danger. Besides, the government is expected to critically follow whether the wet

coffee processing industry owners are implementing the regulation (coffee quality control and transaction), and proclamations (to provide for coffee quality control and marketing) or not. In addition, the government (particularly, ministry of agriculture and Ethiopian EPA) should demonstrate and encourage them to construct wastewater stabilization ponds (instead of disposal pits) to treat the wastewater created by these wet coffee processing industries by considering the amount of wastewater released and carrying capacity of these ponds having different cells (anaerobic, facultative and maturation ponds).

3. Fermentation, pervaporation, composting, co-composting and pyrolysis of coffee waste fractions (husk, pulp, silver skin, and parchment) can be feasible technologically if applied in Ethiopia. Besides, composting, co-composting and pyrolysis technologies can be profitable and implemented easily. However, concerning the spent coffee, applying these technologies in Ethiopia may not be completely sustainable since half of the produced Ethiopian coffee is exported to different countries: the major markets for Ethiopian coffee are the EU (about half of exports), East Asia (about a quarter), and North America. Thus, spent coffee may not be available abundantly relative to the amount produced inside the country. However, by organizing youth groups, microenterprises, who are focusing on the collection of the spent coffee (from the local coffee consumers: residential houses, cafeterias, hotels, and institutions), it is possible to make the technology sustainable. There are many ways to collect spent coffee from the residential houses. Some of these mechanisms are:
    A) Awaring the community about the importance and management methods (including the source segregation of the spent coffee).
    B) Establishing microenterprises at different places, particularly composed of youngsters, job seekers, farmers, etc.
    C) Soliciting the full support and agreement of community leaders such as “kebele” representatives, school community leaders, religious leaders, etc. For this purpose, the role and contribution of local communities and community leaders/representatives is crucial.

4. The chemical composition of coffee waste fractions varies from plant to plant, and within different parts of the same plant. It also varies within plants from different geographic locations, ages, climate, and soil conditions. Thus, future studies should focus on the detailed chemical composition study of all the different fractions of coffee byproducts. Besides, the hydrolysis results of dried coffee pulp indicate that the hydrolysate is composed of more of xylose and arabinose than glucose. Therefore, to produce more ethanol, future studies should focus on strains that can utilize arabinose effectively.
5. The results of the investigation also demonstrate that coffee husk and spent coffee can be used as an alternative substrate for ethanol production, in comparison to different biomass resources (for instance: barley straw, 10 g/L; wheat stillage, 11 g/L; sweet sorghum bagasse, 16.2 g/L; corn stover, 16.8 g/L; wheat straw, 18.1; Korean food waste leachate, 24.17 g/L; and kitchen waste, 30 g/L). This result is very promising and could be improved further by using distillation and hydrophilic membranes for pervaporation. Further research is also needed to examine the economic viability of the process. To study the economic feasibility, the following could be addressed:
    - ❖ LCA (Life Cycle Assessment), which takes into account all the resources and energy inputs required to make a product, the byproducts, and the health and ecological burdens associated with the product;
    - ❖ Applying the biorefinery concept, which addresses the issues: how to utilize, inedible lignocellulosic biomass to produce biofuels, cellulose, hemicellulose, lignin, and byproducts;
    - ❖ Implementing a waste management process, which is fundamental to have a systemic view of the whole process, starting from the collection, including storage and transportation, extraction/recovery of valuable components under the most adequate route, removal of potential contaminants, and finally the recovery of the least valuable materials, resulting in a stream of residues, possibly with some energy content. This approach leads to job creation, increasing the yield and to extend the life of the original materials that will possibly be used for processing more raw-materials, incorporating products

from waste treatment in a more sustainable manufacture of new products, developing a circular economy.

6. The composting process is highly affected by seasonal variation. Thus, it is important to repeat the composting activity in different seasons of the year. Further studies are also highly encouraged to confirm the germination, growth, and yield productivity of matured composted samples by using different seeds. Furthermore, before producing and applying compost samples on soil, first of all, the chemistry of the local soil should be studied in detail. In this regard, the government, the relevant stakeholders, and professionals in the field should assist/encourage and increase the awareness level of the local farmers using composts and associations/microenterprises producing and selling compost.
7. Nutrients found in compost are available in organic form and thus released slowly as the compost decomposes. Thus, future studies should focus on the evaluation of the germination, growth, and yield productivity of matured composted samples for different seeds in different years after applying the compost samples.
8. The chromatogram of the thermal desorption gas chromatography-mass spectrometry (GC/MS) and pyrolysis gas chromatography-mass spectrometry (GC/MS) after desorption results (for husk and pulp) indicated that there are a number of compounds having added value in the chromatograms. Thus, for different coffee waste fractions (including husk and pulp), further studies should focus on detailed analysis of the most significant compounds (peak area, compound name and its % content) should be listed with their relative amount in % and then grouped compounds.

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Appendix

Table A1 Guidelines for Ambient Environmental Standards for Ethiopia and US-EPA Standards for Discharge of Environmental Pollutants

Parameter	**Ambient Environment Standards for Ethiopia: Water Quality Standards (Surface Waters)**	**US-EPA Standards for Discharge of Environmental Pollutants to Inland Surface Waters**
BOD_5	$\leq$ 5 mg/L	30 mg/L, max (3 days at 27ºC)
COD, mg/L		Max 250
Conductivity	1000 µS/cm at 20^0c	
DO	Min 4-6	
NO_3^-	50 mg/L	10 mg/L
NO_2^-	0.1 mg/L	
Nitrogen	1 mg/L (Kjeldahl Nitrogen)	100 mg/L, max (Total nitrogen as N)
Ammonical nitrogen		Max. 50 mg/L, (as N)
pH	6-9 (but no change of more than 0.2 units from natural level)	5.5 to 9.0
SO_4^{2-}	200 mg/L	
Dissolved phosphates (as P)		Max. 5.0 mg/L
Temperature	Discharge must not result in variation of more than 1.5 ℃ - 3 ℃ temp downstream of thermal discharge.	Shall not exceed 5 ºC above the receiving water temperature

TSS	$\leq$ 25 mg/L (annual mean) and 50 mg/L (max value)	100

Source: (EFEPA, 2003) and (US-EPA, 1989)

Table A2: GC-MS results for husk

	Husk	Thermal Desorption 100 > 350°C
Scan number	**Identified compound**	
315	Furanmethanol	
355	Dimethylpyrazool	
539	2-Hydroxy 2-cyclopenten-1-one	
611	1,2-Cyclopentaandione	
632	Methylfurfuraldehyde	
674	2,5-Dimethyl-2,4-dihydroxy-3(2H)-furanone	
746	Phenol	
752	1,2-Cyclohexaandione	
822	2-Hydroxy-3-methylcyclopent-2-en-1-one	
832	Limonene	
934	2-Methoxyphenol	
981	Maltol	
1029	3-Pyridinol	
1037	3-Hydroxy-2,3-dihydromaltol	
1063	1H-Pyrrole-2-carbonitrile	
1080	C2:0-substituted phenol	
1089	Benzoic acid	
1161	4-Methoxyphenol	
1163	2,3-Dihydrobenzofuran	
1176	5-Hydroxymethylfurfuraldehyde	
1181	Benzenepropanenitrile	
1221	C4:0-substituted pyridine	

1225	Niacyne
1232	4-ethyl 2-methoxyphenol
1248	2,3-Dihydro indenone
1257	3-Methyl 4-methoxyphenol
1272	Indol
1286	1,4-Benzenediol
1287	2-Methoxy 4-vinylphenol
1307	Pyrrool 2-carboxamide
1336	2,6-Dimethoxyphenol
1343	2-Propenyl-6-methoxyphenol
1367	Methyl 1,4-benzenediol
1393	1,4-Benzenediol monoacetate
1400	Methylindol
1412	4-Hydroxy 3-methoxybenzaldehyde
1414, 1473	Isoeugenol
1422	3-Methoxy 1,4-benzenzediol + 2- Hydroxyacetophenone
1454	4-Hydroxybenzoic acid methylester
1461	Trimethoxybenzene
1470	4-Ethyl 1,3-benzenediol
1488	Dimethylbenzylalcohol
1515	3,3-Dimethyl isobenzofuranone
1523	4-Hydroxy 3-methoxyacetophenone +
1528	$C_{15}H_{32}$
1559	Methyl trimethoxybenzene
1572	1-(4-Hydroxy-3-methoxy-phenyl)-propan-2-one
1594	4-Hydroxybenzoic acid methylester
1611	3,5-Dimethoxy acetophenone
1711	Propenyl dimethoxyphenol
1729	4-Hydroxy 3,5-dimethoxybenzaldehyde
1772	2,6-Dimethoxy 4-(2-propenyl) phenol

1809	4-Hydroxy 3,5-dimethoxy acetophenone
1835	4-((1E)-3-Hydroxy-1-propenyl)-2-methoxyphenol
1921	6,10,14-Trimethyl-2-pentadecanone
1948	Caffeine
1984	Pentadecanenitrilebranched
2006	Methylpalmitate
2014, 2032, 2339	Pyrazoolderivate
2053	Palmitic acid
2142	Heptadecanoic acid
2172	Methyllinolenate
2177, 2183	Methyloleate
2201	Methylstearate
2214	Linolenic acid
2219	Oleic acid
2238	Stearic acid
2256	Hexadecaneamide
2286	N-methyl hexadecaneamide
2318	N,N-dimethyl hexadecaneamide
2355	$C_{23}H_{48}$
2368	Aliphatic nitrile
2379	Eicosanoic aid methylester
2413	Eicosanoic acid
2435	Octadecaneamide
2444	3-Benzylhexahydropyrrolo[1,2-a] pyrazine-1,4-dione
2464	Heneicosanoic acid methylester
2537	Eicosanoic nitrile
2543	Docosanoic methylester
2549	Bis (2-ethylhexyl) phtalate
2597, 2726	Fatty acid amide
2617	Tricosanoic acid methylester

2661	$C_{27}H_{56}$
2679	Tetracosanoic methylester
2721	$C_{28}H_{58}$
2778	$C_{29}H_{60}$
2861, 2870	Tocopherol
2865	Stigmasta-5,22-dien-3-ol, acetate
2899	Stigmastan-3,5-diene
2994	Ergost-5-en-3-ol
3012	Stigmasterol
3054	Sitosterol
3135	Stigmast-4-en-3-on

Table A3: Results of husk Pyrolysis GC-MS chromatograms

Husk	Pyrolysis 1 min. @ 550°C
Scan number	**Identified compound**
182	CO_2
254	2-Butanone
257	Methylfuran
289	Cyclohexadiene
309	Benzene
331	2-Pentanone
350	Dimethylfuran
408	Pyridine
412	Pyrrool
434	Toluene
463	2-Hexanone
468	Cyclopentanone
478, 796	C3:0-gesubstitueerd furan
509, 586	Methylpyridine
534	2-Cyclopenten-1-one
542, 555	Methylpyrrool
560	Methylcyclopentanone
569	2-Heptanone
581, 597, 633	Xylene
606	Hexaannitrile
626	C_9H_{18}
631	Styrene
640	C_9H_{20}
651	2-Methyl 2-cyclopenten-1-one

660	Acetylfuran
664	Butyrolacton
671	Methoxyphenol
679, 684, 689, 702, 715, 723	C2:0-substituted pyrrool
696, 716	C2:0-substituted pyridine
710	Ethylcyclopentanone
716	Dimethyl cyclopentanone
734, 747, 751, 760, 776, 803, 847	C3:0-gesubstitueerd benzene
740	Cyclicli hycrocarbon MW 136
751	Methyl cyclopentenone
776	Aniline
788	Phenol
806, 843, 852, 894, 903, 923	C4:0-substituted benzene
804, 807, 812, 856, 871	C3:1-substituted benzene
806	$C_{10}H_{22}$
814, 828	$C_{10}H_{20}$
815, 833	C3:0-substituted pyrrool
831	C3:0-substituted pyridine
859	Limonene
868, 933	C2:0-substituted 2-cyclopenten-1-one
884	C4:0-substituted pyrrool
888	Inden
905, 942	Methylphenol
923	Acetophenone
952	4-Methoxyphenol

956, 1012, 1038	C4:1-gesubstitueerd benzene
957	N-methyl succinic imide
962	2-Methyl isocyanobenzene
966	$C_{11}H_{24}$
988, 1034, 1055, 1081, 1086, 1097, 1224	C2:0-substituted phenol
990	Methylbenzofuran
1001	2-Methylbenzoxazool
1006	Cyclic hydrocarbon MW 134
1054, 1065	Methylinden
1061, 1074	C5:0-substituted benznen
1105, 1137, 1168, 1178, 1184, 1216, 1230, 1235, 1244	C3:0-substituted phenol
1105	Dimethoxybenzene
1107, 1126, 1140	$C_{12}H_{24}$
1111	Methoxy methylphenol
1115	Naphtalene
1119	$C_{12}H_{26}$
1140, 1151, 1155	C2:0-substituted benzofuran
1173	Dimethylbenzoxazool
1194	Methylindol
1220, 1226, 1232	Methyl dihydroinden
1221	C6:0-substituted benzene
1226	C3:0-substituted methoxybenzene
1235	C2:0-substituted ethoxyphenol
1252	2,3-Dihydro inden-1-one
1252, 1269	$C_{13}H_{26}$
1263	$C_{13}H_{28}$

1274	Indol
1277, 1299	Methylnaphtalene
1283	$C_{13}H_{26}$
1315	C3:0-substituted benzimidazol
1337	C2:0-substituted indol
1344	Methoxy dihydronaphtalene
1378	C3:0-substituted inden
1389, 1405, 1419	$C_{14}H_{28}$
1390	Biphenyl
1399	$C_{14}H_{30}$
1412, 1428, 1444, 1450, 1472, 1475, 1491	C2:0-substituted naphtalene
1493	C8:0-substituted benzene
1518, 1533, 1548	$C_{15}H_{30}$
1522	C3:0-substituted benzonitrile
1528	$C_{15}H_{32}$
1553, 1574, 1586, 1592, 1604, 1611, 1623, 1629, 1646, 1656	C3:0-substituted naphtalene
1572, 1587	Naphtalenol
1623	C9:0-substituted benzene
1641, 1669	$C_{16}H_{32}$
1650	$C_{16}H_{34}$
1656	Fluorene
1671, 1689, 1697, 1702, 1716, 1726, 1745, 1749, 1766, 1792, 1805, 1823,	C4:0-substitutednaphtalene

1834	
1747, 1758	$C_{17}H_{34}$
1765	$C_{17}H_{36}$
1778, 1861	C11:0-substituted benzene
1796	Methylfluorene
1868, 1880	$C_{18}H_{36}$
1875	$C_{18}H_{38}$
1887	Phenanthrene
1900	Anthracene
1939	Caffeine
1951	Nitroso carbazool
1974	$C_{19}H_{38}$
1980	$C_{19}H_{40}$
1983	Hexadecanenitrile
2005, 2012	Methyl phenantrhene
2024, 2030, 2036	Methyl anthracene
2022, 2060, 2066	Methyl carbazool
2052	Tetramethyl xanthine
2074, 2085	$C_{20}H_{40}$
2080	$C_{20}H_{42}$ + 1-Methyl-9H-pyrido[3,4-b]indol
2115, 2123, 2129	C2:0-substitutedphenanthrene
2141, 2147, 2154,	C2:0-substituted anthracene
2161, 2193	
2162, 2165, 2170	Octadecene nitrile
2176	$C_{21}H_{44}$
2184	Octadecane nitrile
2251	C3:0-substituted phenanthrene
2253	Hexadecane amide
2268	$C_{22}H_{46}$
2285	N-methyl fatty acidamide

2355	$C_{23}H_{48}$
2368	Nonadecane nitrile
2440	$C_{24}H_{50}$
2521	$C_{25}H_{52}$
2531	Chrysene
2537	Eicosane nitrile
2675	$C_{27}H_{56}$
2694	Heneicosane nitrile
2746	$C_{28}H_{58}$
2932	Stigmastan-3,5-diene

Table A4: GC-MS results for coffee pulp

Coffee pulp	Thermal Desorption 100 > 350°C
Scan number	**Identified compound**
232	Acetoxyacetone
403	Xylene
512	Cyclohexanone
704	Phenol
787	Limonene
910	Methoxyphenol
912	Methylphenol
967	Methylbenzoxazool
1010	Benzylnitrile
1016	4-Pyridone
1037	Succinimide
1040, 1071, 1116	C2:0-gesubstitueerd phenol +
1054	1H-Pyrrool-2-carbonitrile
1062	1,2,4-Triazine-3,5(2H,4H)-dione
1087	Benzoic acid +
1096	2-Methoxy 5-methylphenol
1156	Dianhydro-α-d-glucopyranose
1159	2,3-Dihydrobenzofuran
1175	Benzeenpropane nitrile
1227	2-Methoxy 4-ethylphenol
1237	3,4-Dimethyl-3-pyrrolin-2-on
1258	$C_{13}H_{28}$
1268	Indol
1281	1,4-Benzenediol
1284	2-Methoxy 4-vinylphenol

1297	Alkyl-substituted dihydropyran-2-one
1333	2,6-Dimethoxyphenol
1341	Eugenol
1348	$C_{14}H_{30}$
1367	Methyl dihydroxybenzene
1391	4-Propoxyphenol
1398	Methylindol
1409	3-Hydroxy 4-methoxybenzaldehyde
1412, 1471	Isoeugenol
1460	Trimethoxybenzene
1513	6-Methoxy methylbenzofuran
1521	2-Methoxy 5-acetoxyphenol
1527	$C_{15}H_{32}$
1571	4-Hydroxy-3-methoxyphenyl acetone
1611	Dimethoxyacetophenone
1651, 1772	Methoxy eugenol
1710	2,6-Dimethoxy 4(2-propenyl)phenol
1728	3,5-Dimethoxy 4-hydroxybenzaldehyde
1734	2-Methyl-4-(phenylmethylene)oxazol-5(4H)-on
1765	$C_{16}H_{34}$
1808	2,6-Dimethoxy 4-acetoxyphenol
1821	3-Methoxy-4-hydroxycinnamaldehyde
1835	Tetradecanoic acid
1864	Hexahydropyrrolo[1,2-α] pyrazine-1,4-dione
1875	$C_{17}H_{36}$
1904	Pentadecanoic acid
1912, 1921, 1943, 2010, 2027, 2041, 2319, 2336	Pyrazinederivate
1921	6,10,14-Trimethylpentadecan-2-one

1983	Hexadecane nitrile
1988	Tetradecylfuran
2005	Methyl hexadecanoate
2022	16-Hydroxy 4-hexadecene acid lacton
2048	Hexadecanoic acid
2080	$C_{20}H_{42}$
2085	1-Methyl-9H-pyrido [3,4-b] indol
2101	9H-Pyrido [3,4-b] indol
2121, 2302, 2360, 2414, 2740	Fatty acid ramide
2141	Heptadecanoid acid
2153	Hexadecanoic acid 2-propenylester
2176	$C_{21}H_{44}$
2184	Octadecane nitrile
2200	Methyl octadecanoate
2210	Octadecadiene acid
2216, 2220	Octadecene acid
2237	Octadecane acid
2254	Hexadecane amide
2267	$C_{22}H_{46}$
2285	N-methyl hexadecane amide
2351	$C_{23}H_{46}$
2355	$C_{23}H_{48}$
2368	Nonacosane nitrile
2408, 2443	3-Benzylhexahydropyrrolo[1,2-α] pyrazine-1,4-dion"
2418	Octadecene amide
2434	Octadecane amide
2440	$C_{24}H_{50}$
2517	$C_{25}H_{50}$

2521	$C_{25}H_{52}$
2537	Eicosanenitrile
2544	Methyl docosanoate
2599	Eicosane amide
2617	Heneicosane nitrile
2672	$C_{27}H_{56}$
2689	Docosane nitrile
2734	$C_{28}H_{58}$
2791	Ergost-5-en-3-ol acetate
2793	$C_{29}H_{60}$
2806	4,4-Dimethylcholesta-6,22,24-triene
2840, 2893, 2914	Stigmastan-3,5-diene
2866	Ergost-5-en-3-ol acetate
2880	Stigmasta-5,22-dien-3-ol acetate
2905	$C_{31}H_{64}$
3120	Stigmasta-3,5-dien-7-one
3151	Stigmast-4-en-3-on

Table A5: Results of coffee pulp Pyrolysis GC-MS chromatograms

Coffee pulp	Pyrolysis 1 min. @ 550°C
Scan number	**Identified compound**
179	CO_2
197	Butene
218	Pentene
255	Methylfuran
257	Acetic acid
309	Benzene
348	Dimethylpyrazol
372	2-Methylbutane nitrile
383	3-Methylbutane nitrile
390	1-Methylpyrrol
403	Pyridine
412	Pyrrol
433	Toluene
462	Methylpyruvate
477	C3:0-substituted furan
482	C_8H_{18}
496, 677, 683, 700, 714, 722	C2:0-substituted pyrrol
506, 581	Methylpyridine
531	2-Cyclopenten-1-one
532	Furfuraldehyde
541, 553	3-Methylpyrrol
568	C_9H_{20}
579, 595	Xyleen

613, 694, 714	C2:0-gesubstitueerd pyridine
630	Styrene
640	C_9H_{20}
649	Methyl 2-cyclopenten-1-one
687	2-Hydroxy 2-cyclopenten-1-one
705, 805	$C_{10}H_{22}$
720, 807, 810, 855, 871	C3:1-substituted benzene
729, 814, 832, 846	C3:0-substituted pyrrol
750	3-Methyl 2-cyclopenten-1-one
788	Fenol
791	$C_{10}H_{20}$
801	C3:0-substituted benzene
829	2-Aminopyridine
840, 909, 966	$C_{11}H_{24}$
842, 851, 932	C4:0-substituted benzene
852	3-Methyl 1,2-cyclopentane dione
858	Limonene
868	2,3-Dimethyl 2-cyclopenten-1-one
883, 930	C4:0-substituted pyrrol
887	Inden
895	$C_{11}H_{22}$ + 3-Methoxy 4-methyl 2-cyclopenten-1-one
905, 939, 945	Methylphenol
918	2-Acetylpyrrol
921	Acetophenone
932	3-Ethyl 2-cyclopenten-1-one
951	C3:0-gesubstitueerd 2-cyclopenten-1-one
957	N-methyl succinic ommide
988, 1034, 1047,	C2:0-substituted phenol

1053, 1083, 1098, 1125	
989	Methylbenzofuran
1000	2-Methyl benzoxazool + 5-Methyl 2-pyridinamide
1012, 1052	C4:1-substituted benzene
1016	4,4-Dimethyl 2-cyclohexen-1-one
1042	Succinic imide
1064	Methylinden + Pyrrol carbonitrile
1073	C5:0-substituted benzene
1106	$C_{12}H_{24}$
1111	Methyl methoxphenol
1114	Naphtalene + Glutaric imide
1118	$C_{12}H_{26}$
1145	C3:0-substituted imidazol
1154	C2:0substituted benzofuran
1167	2,3-Dihydrobenzofuran
1168, 1185, 1217	C3:0-substituted phenol
1172	C2:0-substituted benzoxazol
1185	Benzeenpropane nitrile
1194, 1205, 1399	Methylindol
1220, 1230	Methyl dihydronaphtalene
1220	C6:0-substituted benzene
1235	4-Ethyl 2-methoxyphenol
1251	$C_{13}H_{26}$ + 2,3-Dihydro 1-inden-1-on
1262	$C_{13}H_{26}$ + 2,3-Dihydro 1-inden-1-on
1272	Indol
1276, 1298	Methylnaphtalene
1288	2-Methoxy 4-vinylphenol
1337, 1532	C2:0-substituted indol
1343	C3:0-substituted benzimidazol

1350, 1399	$C_{14}H_{30}$
1378	Trimethylinden
1388, 1418	$C_{14}H_{28}$
1410, 1427, 1443, 1449, 1471, 1473, 1490	C2:0-substituted naphtalene
1460	Trimethoxybenzene
1481, 1527	$C_{15}H_{32}$
1493	C8:0 substituted benzene
1518, 1548	$C_{15}H_{30}$
1521	Trimethylbenzonitrile
1528	C2:0-substituted indolizine
1553, 1573, 1577, 1585, 1591, 1603, 1610, 1622, 1628, 1646, 1655	C3:0-substituted naphtalene
1641	$C_{16}H_{32}$
1649	$C_{16}H_{34}$
1695, 1728	Methyl naphtalenol
1703	$C_{18}H_{38}$
1740, 1747, 1757, 1769	$C_{17}H_{34}$
1744	C10:0-substituted benzene
1765	$C_{17}H_{36}$
1860	C11:0-substituted benzene
1868	$C_{18}H_{36}$
1875	$C_{18}H_{38}$
1885	Phenanthrene
1898	Anthracene
1936	9H-Carbazool-9-methanol

1973	$C_{19}H_{38}$
1980	$C_{19}H_{40}$
1982	Hexadecane nitrile
2004, 2010, 2021	Methylphenanthrene
2029, 2035	Methylanthracene
2038	Pyrazine derivate
2044	Hexadecanoic acid
2056	Methylcarbazol
2074, 2084	$C_{20}H_{40}$
2079	$C_{20}H_{42}$
2095	9H-Pyrido[3,4-b]indol
2140, 2145, 2152	C2:0-substituted phenanthrene
2170	$C_{21}H_{42}$
2175	$C_{21}H_{44}$
2183	Octadecane nitrile
2192	C2:0-substituted anthracene
2252	Hexadecanoic amide
2262	$C_{22}H_{44}$
2267	$C_{22}H_{46}$
2284	N-methyl hexadecane amide
2294	Benzo[b]nafto[2,3-d]furan
2350	$C_{23}H_{26}$
2355	$C_{23}H_{48}$
2367	Nonadecane nitrile
2404	2H-Phenanthro[9,10-α] pyran
2432	Octadecanoic amide
2435	$C_{24}H_{48}$
2439	$C_{24}H_{50}$
2517	$C_{25}H_{50}$
2520	$C_{25}H_{52}$

2537, 2617, 2692, 2758, 2819, 2872	Aliphatic nitrile
2595	$C_{26}H_{52}$
2599	$C_{26}H_{54}$
2670	$C_{27}H_{54}$
2673	$C_{27}H_{56}$
2738	$C_{28}H_{56}$
2740	$C_{28}H_{58}$
2799	$C_{29}H_{58}$
2800	$C_{29}H_{60}$
2855	$C_{30}H_{60}$
2857	$C_{30}H_{62}$
2911	$C_{31}H_{62}$
2912	$C_{31}H_{64}$
2967	$C_{32}H_{64}$
2968	$C_{32}H_{66}$

List of Scientific Contributions

Articles in internationally peer-reviewed academic journals

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- Tadesse Getahun, Embialle Mengistie, Alemayehu Haddis, Fantahun Wassie, Esayas Alemayehu, **Dessalegn** Dadi, Tom Van Gerven, Bart Van der Bruggen (2012). Municipal solid waste generation in growing urban areas in Africa: current practices and relation to socioeconomic factors in Jimma, Ethiopia. *Environmental Monitoring and Assessment,* 184: 6337-6345.
- Asmamaw Abera, **Dessalegn** Dadi, Tadesse Getahun, Yohannes Tefera (2016). Heavy metal content and physico chemical properties of soil around solid waste disposal sites. *American Journal of Scientific and Industrial Research,* 7(5) 129-136.
- **Dessalegn** Dadi, Abebe Beyene, Kenneth Simoens, Jimmy Soares, Mekonnen Demeke, Johan Thevelein, Patricia Luis, Bart Van der Bruggen (2017). Valorization of coffee byproducts for bioethanol production using lignocellulosic yeast fermentation and pervaporation. *International Journal of Environmental Science and Technology* (Article in press).
- **Dessalegn** Dadi, Embialle Mengistie, Gudina Terefe, Tadesse Getahun, Alemayehu Haddis, Wondwossen Birke, Abebe Beyene, Patricia Luis, Bart Van der Bruggen (2017). Assessment of the effluent quality of wet coffee processing wastewater and its influence on downstream water quality. *Journal of Ecohydrology and Hydrobiology* (Article in press).
- Mónica Hernández Rodríguez, Jan Yperman, Robert Carleer, Jens Maggen, **Dessalegn** Dadi, Grazyna Gryglewicz, Bart Van der Bruggen, José Falcón Hernandez, Alexis Otero Calvis (2018). Adsorption of Ni (II) on spent coffee and coffee husk based activated carbon. *Journal of Environmental Chemical Engineering* 6, 1161-1170.

Contributions to international scientific conferences

- **Dessalegn** Dadi, Abebe Beyene, Kenneth Simoens, Jimmy Soares, Mekonnen Demeke, Johan Thevelein, Patricia Luis, Bart Van der Bruggen (2017). Bioethanol production from coffee waste fractions and quality upgrading using an alcohol selective pervaporation membrane. The African Membrane Society on Membrane Technologies for Water Treatment in Urban Centers and Small Communities; First Bioannual International conference, Sfax, Tunisia, May 3rd-5th 2016.

About the author

Dessalegn Dadi Olani was born in Kombosha, Guduru district of Oromia regional, national state, Ethiopia in 1978. He did his diploma study in Chemistry at Jimma Teachers college, Jimma, Ethiopia and graduated in July 1998. In August 1998 he has been employed in Habro district educational office of West Hararghe zone as a full-time teacher. After 2 years of service, he has got a chance to proceed with his Bachelor degree in chemistry at Haramaya University, Ethiopia and graduated in November 2004. Then, he served again for one year and has got a chance to proceed with his M.Sc degree study at Addis Ababa University, Ethiopia and graduated with environmental science in March 2008. Afterwards, he returned back to Chiro (Asebe Teferi) preparatory school of West Hararghe zone educational office and taught for 6 months. In October 2008, he has got the chance to be recruited at the rank of lecturer position at the environmental health sciences and technology department of Jimma University, Ethiopia. In October 2013, he has got the chance to proceed with his pre-doctoral Ph.D. study for 4 months at University of Leuven, Belgium under the promotership of Prof Bart Van der Bruggen, Prof. Patricia Luis, and Dr. Abebe Beyene, and finished it successfully. Again in March 2014, he has been admitted by Arenberg doctoral school of KUL as a joint/dual Ph.D. student in between Jimma University and University of Leuven; and the financial budget was funded by the Flemish Institutional University Cooperation and Jimma University partnership program (VLIR-UOS IUC project). The main focus of his Ph.D. study is Valorization of coffee byproducts via biomass conversion technologies. During the course of his Ph.D. study, he has attended several training and skill courses organized by KUL. Besides, he has actively participated and orally presented part of his Ph.D. study at the international conference organized by "The African Membrane Society" on *Membrane Technologies for Water Treatment in Urban Centers and Small Communities; First Biannual International conference*, which was held in Sfax, Tunisia, May 3rd-5th 2016. Since 2016, he has been an active member of the African Membrane Society (AMS). These experiences helped him to think critically, design and conduct an independent research, which can solve problems and arrive at better scientific solutions. Currently, he is working at the environmental health sciences and technology department of Jimma University, Ethiopia. Besides, for the year 2018-2020, he is working as a board

member of African Membrane Society International Congress (AMSIC) at the position of co-director of external relations.

Re: Revised version of the thesis

Patricia Luis Alconero <patricia.luis@uclouvain.be>

Thu 2/8/2018 10:34 AM

To: Bart Van der Bruggen <bart.vanderbruggen@kuleuven.be>; Dessalegn Dadi Olani <dessalegndadi.olani@kuleuven.be>; abebe.beyene@gmail.com <abebe.beyene@gmail.com>;

ok for me too!

Patricia Luis
Materials & Process Engineering (iMMC-IMAP)
Université catholique de Louvain, Belgium
Place Sainte Barbe 2, 1348 Louvain-la-Neuve
Tel: +32 (0)10 472402; Mobile: +32 485 950144; Fax: +32 (0)10 474028

From: Bart Van der Bruggen <bart.vanderbruggen@kuleuven.be>
Sent: 08 February 2018 10:32
To: Dessalegn Dadi Olani; Patricia Luis Alconero; abebe.beyene@gmail.com
Subject: Re: Revised version of the thesis

OK for me - time to send it!

Bart Van der Bruggen
KU Leuven - department of Chemical Engineering
Not available by phone

"A (wo-)man who dares to waste one hour of time has not discovered the value of life" (Charles Darwin)

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From: Dessalegn Dadi Olani
Sent: 08 February 2018 10:26
To: Bart Van der Bruggen; patricia.luis@uclouvain.be; abebe.beyene@gmail.com
Subject: Re: Revised version of the thesis

Dear Prof. Bart,
Your key suggestion is incorporated!!!

With best regards,

++
Dessalegn Dadi Olani

Process Engineering for Sustainable Systems (ProcESS)
Department of Chemical Engineering - KU Leuven

Room 04.115, Celestijnenlaan 200F , 3001 Leuven, BELGIUM
Alternate email: dessalegndadiolani@gmail.com
Tel.: (+32) 16.32.27.16, Mobile: (+32) 486.811.524

From: Dessalegn Dadi Olani
Sent: Thursday, February 8, 2018 9:50 AM
To: Bart Van der Bruggen; patricia.luis@uclouvain.be; abebe.beyene@gmail.com
Subject: Re: Revised version of the thesis

Dear Prof. Bart,
Thank you very much for the reminder.
Yes, I fully agree. Their contribution and decision was really crucial!!!

++
Dessalegn Dadi Olani

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From: Bart Van der Bruggen
Sent: Thursday, February 8, 2018 9:43 AM
To: Dessalegn Dadi Olani; patricia.luis@uclouvain.be; abebe.beyene@gmail.com
Subject: Re: Revised version of the thesis

Just one thing... you actually don't mention the people involved with VLIR-UOS as such, perhaps this should be a bit more visible? In the acknowledgement; I would also include the coordinators, prof. Luc Duchateau and Kora - after all, they agreed with one 'extra' PhD that was not planned...

Bart

Bart Van der Bruggen
KU Leuven - department of Chemical Engineering
Not available by phone

"A (wo-)man who dares to waste one hour of time has not discovered the value of life" (Charles Darwin)

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From: Dessalegn Dadi Olani
Sent: 08 February 2018 09:06
To: Bart Van der Bruggen; Bart Van der Bruggen; patricia.luis@uclouvain.be; abebe.beyene@gmail.com
Subject: Re: Revised version of the thesis

Dear my promoters,
In the attachment, you will find the modified version of the thesis.
If you have suggestion and observe something which I have overlooked it, please, let me know it in advance!

With best regards,

++
Dessalegn Dadi Olani

Process Engineering for Sustainable Systems (ProcESS)
Department of Chemical Engineering - KU Leuven

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From: Dessalegn Dadi Olani
Sent: Tuesday, February 6, 2018 6:48 PM
To: Bart Van der Bruggen; Bart Van der Bruggen; patricia.luis@uclouvain.be; abebe.beyene@gmail.com
Subject: Re: Revised version of the thesis

Dear Prof. Bart,
Thank you very much.
For sure, I will incorporate all the forwarded crucial comments/suggestions.

With best regards,

++
Dessalegn Dadi Olani

Process Engineering for Sustainable Systems (ProcESS)
Department of Chemical Engineering - KU Leuven

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Alternate email: dessalegndadiolani@gmail.com
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From: Bart Van der Bruggen
Sent: Tuesday, February 6, 2018 5:35 PM
To: Dessalegn Dadi Olani; Bart Van der Bruggen; patricia.luis@uclouvain.be; abebe.beyene@gmail.com
Subject: Re: Revised version of the thesis

Dessalegn,

- On the 'Dedication' page, first point, add a full stop after the sentence.
- page 11: AMSIC - capitalize each word
- consider numbering the first 15 pages (with abbreviations, table of contents,...) with Latin numbering (I, II, II, IV, V,...)
- page 11 now in the full text, caption: ...of the pervaporation process
- p49 table 3.1 - the p-values that are zero, should they in fact not be <0.0001?
- p77 a similar remark for the 0.00 standard deviations (and p81)
- Table 4.4 remove the initial of the authors ("Belkacami et al. (2002)'
- p85: change "While, as indicated in Figures 4.2e-h, using both yeasts, partial molar flux and permeance of water is higher than for ethanol. " to "However, as indicated in Figures 4.2e-h, for both yeasts, the partial molar flux and permeance of water iarehigher than for ethanol. "
- p115 change "exaplained before " to "explained" - also change 'The possible' to 'A possible'.
- p118: exactly the same! You did copy-paste! Change the sentence here (you can refer to what was said on p115).
- p128 duartion should be duration
- p131 'inorder' should be 'in order'
- p132 and elsewhere: you use a superscript '0' for the degree symbol. That looks more or less the same but is not correct. If you don't have the correct symbol, you may copy/paste from the first line of p132 where it is correct. In all the red text it is incorrect.
- p140: 'almost in agreement' does not exist, it is either in agreement or not. Here it is so you should delete 'almost'.
- p149 'are summarized' should be 'is summarized'.

Add a full stop after this sentence.
- Caption table 6.5 - pyrolysis without capital
- p150 'sigma-aldrich company '- 'Sigm Aldrich'
- p150 'eventhough' should be 'even though'
- p151 'interms' - in terms
- p155 point 4 has a double stop and p157 point C has no stop at all.

That's all!

Bart Van der Bruggen
KU Leuven - department of Chemical Engineering
Not available by phone

"A (wo-)man who dares to waste one hour of time has not discovered the value of life" (Charles Darwin)

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From: Dessalegn Dadi Olani
Sent: 06 February 2018 11:04
To: Bart Van der Bruggen; Bart Van der Bruggen; patricia.luis@uclouvain.be; abebe.beyene@gmail.com
Subject: Re: Revised version of the thesis

Dear my promoters,
In the attachment, you will find the modified version of the thesis.
In particular, I need your crucial comment/suggestion on the those texts/figures/tables, which are highlighted with red-color.
For your information and action, I inserted the logo of JU in the second cover page of the thesis. Shall I keep it there or move it to another place?

After incorporating your comment/suggestion, and then updating the Table of contents, I am planning to submit the final version on the coming Friday

With kind regards,

++
Dessalegn Dadi Olani

Process Engineering for Sustainable Systems (ProcESS)
Department of Chemical Engineering - KU Leuven

Room 04.115, Celestijnenlaan 200F , 3001 Leuven, BELGIUM
Alternate email: dessalegndadiolani@gmail.com
Tel.: (+32) 16.32.27.16, Mobile: (+32) 486.811.524

From: Dessalegn Dadi Olani
Sent: Friday, February 2, 2018 9:23 AM
To: Bart Van der Bruggen; Bart Van der Bruggen; patricia.luis@uclouvain.be; abebe.beyene@gmail.com
Subject: Re: Revised version of the thesis

Dear Prof. Bart,
Thank you very much and for sure I will do my best.

With kind regards,

Dessalegn

++
Dessalegn Dadi Olani

Process Engineering for Sustainable Systems (ProcESS)
Department of Chemical Engineering - KU Leuven

Room 04.115, Celestijnenlaan 200F , 3001 Leuven, BELGIUM
Alternate email: dessalegndadiolani@gmail.com
Tel.: (+32) 16.32.27.16, Mobile: (+32) 486.811.524

From: Bart Van der Bruggen
Sent: Friday, February 2, 2018 9:11 AM
To: Dessalegn Dadi Olani; Bart Van der Bruggen; patricia.luis@uclouvain.be; abebe.beyene@gmail.com
Subject: Re: Revised version of the thesis

Dessalegn

Another round of corrections. Most are small details but for the pyrolysis chapter I want you to dig a little deeper yet. See my comments.
You still have some time to further correct, and it is important because the final result will go in the history as your thesis.

Bart

Bart Van der Bruggen
KU Leuven - department of Chemical Engineering
Not available by phone

"A (wo-)man who dares to waste one hour of time has not discovered the value of life" (Charles Darwin)

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From: Dessalegn Dadi Olani <dessalegndadi.olani@kuleuven.be>
Sent: 31 January 2018 18:52
To: Bart Van der Bruggen; patricia.luis@uclouvain.be; abebe.beyene@gmail.com
Subject: Revised version of the thesis

Dear my promoters,
In the attachment, you will find the revised version of the thesis for your crucial comments/suggestions.

With kind regards,

Dessalegn

++
Dessalegn Dadi Olani

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